BIOCHARS AS AMENDMENTS FOR SASKATCHEWAN AGRICULTURAL SOILS

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By

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ABSTRACT

Biochars are the product of high temperature treatment of carbonaceous materials with little or no oxygen present, termed "pyrolysis". Biochars derived from the pyrolysis of biomass feedstocks have proven effective amendments on highly weathered tropical soils. However less is known about their impact on temperate soils and associated crop growth. Moreover, there is inadequate knowledge of the impacts of different biochars produced from different feedstocks under differing pyrolysis conditions. Therefore, a study was conducted to evaluate the effectiveness of different biochars as amendments to improve soil conditions for crop growth, with emphasis on soil fertility and crop nutrition impacts. The response of canola-wheat in rotation to five biochars was evaluated in controlled environment and field experiments conducted on Brown and Black Chernozem soils over a two-year period. Treatments were biochar added at 1 and 2 t ha^{-1} without and with nitrogen (N) and phosphorus (P) fertilizers at 50 or 100 kg N ha^{-1} and 25 kg P_2O_5 ha^{-1}. Parameters evaluated were crop biomass and grain yield, N and P uptake, % recovery of applied N and P, residual soil nutrients (NO_3^--N, and PO_4^+-P), pH, electrical conductivity (EC), % organic carbon (% OC) and gravimetric soil moisture. Biochar application resulted in significant increases (p<0.05) in canola yield compared to the control for two fast pyrolysis biochars originating from wheat and flax straw added to the Black Chernozem soil in both studies. No significant response was observed for any of the biochars on the Brown Chernozem. Slow pyrolysis biochar derived from willow feedstock appeared less effective did not show any significant response. Occasional depressions in crop yield were observed in both crops with both soils. In these calcareous Chernozems, biochar did not greatly alter the N and P availability, and its effects on soil pH, % OC, EC and moisture content were small and often non-significant. These results suggest that biochar applications at 1-2 t ha^{-1} to prairie Chernozemic soils will not have large effects on soil properties or plant growth. Higher rates of application will require development of application technology due to the dusty, powdery nature of the biochar material.

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DEDICATION

This thesis is dedicated to my parents Geash Uddin Ahmed and Rizia Khatun who have always been so close to me that I feel them with me whenever I needed them most. It is their unconditional love that motivates me to set higher targets, which has made me the person I am today.

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LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
BC	Black carbon
BET	Brunauer–Emmett–Teller
CB	Central Butte
CB-Brown	Central butte Brown Chernozem soil/site
CEC	Cation exchange capacity
CLC	Conservation learning centre
CLC-Black	Conservation learning centre Black Chernozem soil/site
EC	Electrical conductivity
F	F value/statistics
FC	Field capacity
FSB-Fine	Flax straw fine fraction biochar
GHG	Greenhouse gas
HSD	Honest significant different
MK	Modified Kelowna
NUE	Nitrogen use efficiency
OC	Organic carbon
OM	Organic matter
p	P value/statistics
PA	Prince Albert
SEM	Standard error of mean
SOC	Soil organic carbon
SOM	Soil organic matter
SSA	Specific surface area
TN	Total nitrogen
TOC	Total organic carbon
TS	Total sulfur
VM	Volatile organic matter
WB-Chunky	Willow chunky fraction biochar
WB-Fine	Willow fine fraction biochar
WSB-Chunky	Wheat straw chunky fraction biochar
WSB-Fine	Wheat straw fine fraction biochar

1. INTRODUCTION

1.1 Biochar and Black carbon

Biochar is a carbon (C) rich, predominantly stable organic carbon (OC) compound that is produced when biomass (e.g., agricultural crop residues, wood, waste, etc.) is heated in an oxygen (O_2)-depleted environment (Verheijen et al., 2010). The term "Black Carbon (BC)" is usually used for the carbonaceous solid byproducts of the chemical-thermal conversion of any C containing material that may, or may not, be biomass (Spokas et al., 2012). Specifically, biochar has been used to refer to the material that is produced as a driver of C sequestration from renewable and sustainable biomass (Lehmann, 2007a). Therefore, all biochar is BC, but not all BC is biochar.

Humans started using BC since fire pits were built on soil in the early days of human civilization (Lefroy, 1883; Spokas et al., 2012). During the Neolithic revolution, in the river valleys of Egypt and Mesopotamia, forests were cut; the "slash" permitted to dry, and then burned in the following dry season (Clark, 1952). The resulting ash mixed with BC fertilized the soil, and the burned field was then planted at the beginning of the next rainy season with crops. Historical evidence was found for use of BC in Japan as early as the 1600s and potentially earlier in China (Ogawa and Okimori, 2010). An example of the BC effect on increasing soil fertility is the "Terra Preta" soils of central Amazonia, which are presumably human-made by pre-Columbian native populations (Kleiner, 2009). In 1870, James Orton, an American geologist and explorer, noticed that alongside the typically grey, acidic soils of the basin, there existed large patches of 'black and very fertile' soil (Wayne, 2012). The key ingredient was C. The Terra Preta soils contain up to 9 per cent C, compared with 0.5 per cent in surrounding soils (Wayne, 2012). Terra Preta soils are reported to have a higher nutrient level and a better nutrient retention capacity than surrounding infertile soils (Glaser et al., 2001). The term biochar first appears in the scientific literature around 1998 for the residual of biomass pyrolysis (Bapat and Manahan, 1998).

1.2 Biochar as a soil amendment

Soil amendment with biochar produced from different biomass feedstocks attracted extensive attention in the late 1980's largely because it increases the C sequestered in soils (Kuhlbusch and Crutzen, 1995; Kwapinski et al., 2010) and thereby decreases the amount of CO_2 that enters the atmosphere (Lehmann, 2007a; Novak et al., 2009; Kwapinski et al., 2010).

The production conditions, along with biomass feedstocks, determines the physical and chemical qualities of the produced biochar as a soil amendment (Antal and Gronli, 2003). Application of biochar commonly influences soil bulk density, OC content, ash content, nutrient content, elemental composition, surface area, porosity, surface functional groups, cation exchange capacity (CEC), iodine number, and sorption properties (Gaskin et al., 2009). Upon pyrolysis of biomass feedstock, most biochar retains calcium (Ca), magnesium (Mg), potassium (K) and phosphorus (P) and plant micronutrients, and about half of the nitrogen (N) and sulfur (S) of the biomass feedstock that are partitioned into the biochar fraction (Laird et al., 2010). Therefore, application of biochar to a soil generally returns most of the nutrients back to the soil. Biochar also increases the capacity of soils to adsorb plant nutrients (Lehman et al., 2007; Cheng et al., 2008; Spokas et al., 2012), thereby potentially reducing leaching losses of nutrients.

Biochar has been shown to decrease soil bulk density, and increase CEC, nutrient cycling, and the ability of soils to retain plant available water (Fig. 1). Therefore, the use of biochar as a soil amendment is expected to increase both nutrient and water use efficiency and thereby agronomic crop productivity (Glaser et al., 2001; Liang et al., 2006). In this thesis, this hypothesis is tested for application of biochar to prairie soils differing in OC content. Several reports indicate that soil biochar application alters soil properties and increase crop yields (Lehman, 2006; Chan et al., 2010; Spokas et al., 2012). Much of this work on the impact of biochar on soil quality and agronomic yield has been conducted in the tropics and some in temperate regions. The highly weathered Oxisols and Ultisols of the tropics intrinsically have low nutrient retention capacity due to a dominance of Fe- and Al-oxides and 1:1 phyllosilicates in the clay fraction (Laird et al., 2010). By contrast, temperate soils are typically dominated by 2:1 phyllosilicates clays, have higher levels of soil OM, and higher nutrient and water holding capacities, so responses to biochar amendment are expected to be less.

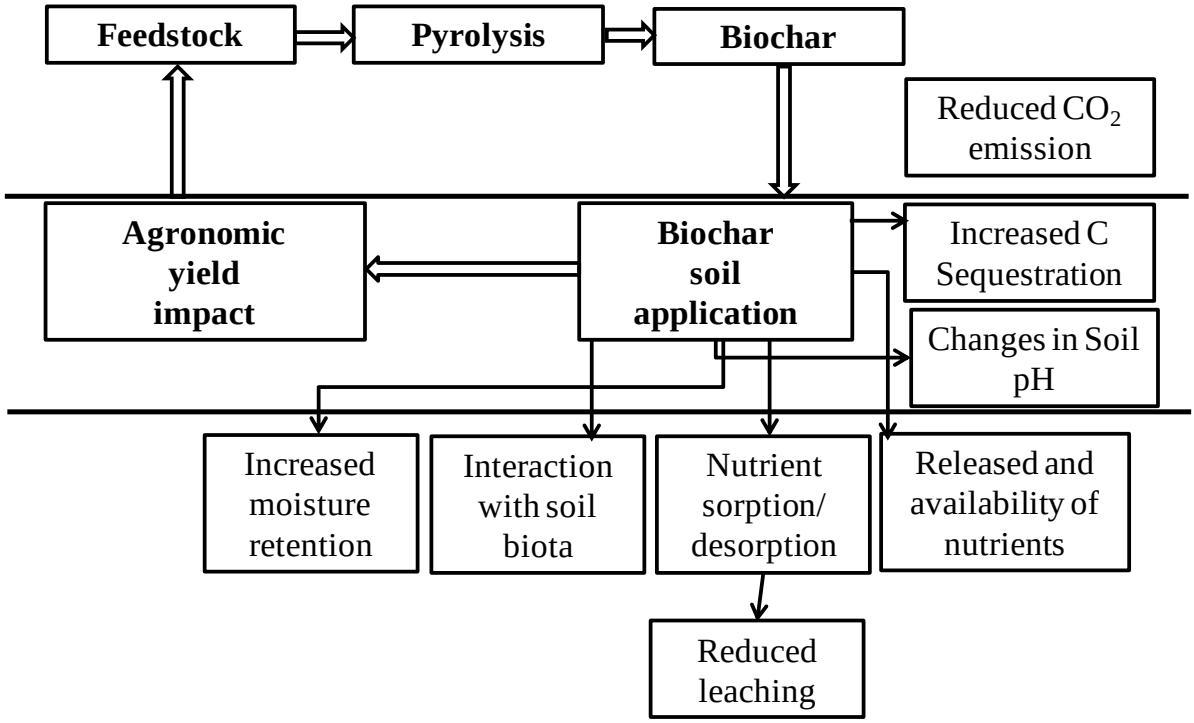

Fig. 1.1. Conceptual framework of using biochar as a soil amendment

1.3 MSc research justification

Nutrient losses prior to plant demand reduce the utilization efficiency of fertilizers applied in agricultural systems. Moreover, excessive loss is regarded as a major contribution to various ecological problems, which may create a hazard to the quality of surface and ground water (Alva et al., 2003; Camargo and Alonso, 2006; Bakhsh et al., 2007). To alleviate this problem, either using slow release fertilizers (Gentile et al, 2009) or increasing adsorption sites (Lehman et al., 2003) could be effective. Additionally, biochar produced from local biomass feedstocks could play a key role in N cycling, especially as related to nutrient retention when applied to the soil (Ding et al., 2010).

To date, most of the studies with biochar have been conducted with very high rates of biochar application (tens to hundreds t ha^{-1}), but such rates may be considered impractical for application of dry chars due to their very low density and powdery nature, making them difficult to transport and apply, especially in the windy southern Canadian prairies. Most of the research to date has focused on nutrient poor soils in sub-tropical and tropical regions, and little is known about the effect on younger soils of the northern Great Plains such as Saskatchewan.

Understanding the characteristics of different biochars and comparison of the effects of biochars on soils and crop yield across the province is needed to better understand the potential benefits of biochar as a soil amendment for the purpose of improving soil quality and plant yield on the Canadian Prairie. The overall objective of this research was to evaluate the effectiveness of different biochars as soil amendments to improve soil conditions for crop growth, with emphasis on soil fertility and crop nutrition impacts.

1.4 Thesis arrangement

Following the introduction (Chapter 1) and literature review (Chapter 2), the research presented in this thesis is a compilation of two manuscripts that cover the effects of application of five different biochars in a canola-wheat rotation grown on two soils (Brown and Black Chernozems) under controlled environment growth chamber (Chapter 3) and field conditions (Chapter 4). A synthesis and conclusion (Chapter 5) are provided at the end.

The general objective of the study was to evaluate the effectiveness of different biochars as soil amendments to improve soil conditions for crop growth, with emphasis on soil fertility impacts. Two soils were chosen for the study to provide a contrast in soil properties, and provide representation of the southern (Brown Chernozem) and northern (Black Chernozem) agricultural regions of Saskatchewan. Chapter 3 covers the effects of amending with five different biochars applied at two rates (1 and 2 t ha^{-1}) on canola and wheat biomass yield, uptake and recovery of N and P in the two contrasting Saskatchewan soils under controlled environment conditions in a growth chamber. The effect of biochars on soil properties, including available nutrients, soil OC, pH and electrical conductivity (EC) were evaluated at the end of the growth period.

In Chapter 4, a field study is reported that addresses the effectiveness of different biochars as soil amendments to improve soil conditions for crop growth, with emphasis on revealing impacts under the variable environmental conditions of the field. Two sites were chosen for the study to provide a contrast in soil properties and provide representation of the southern and northern agricultural regions of Saskatchewan. We investigated the effects of amendment with four different biochars applied at two rates on canola and wheat biomass yield, uptake and % recovery of applied N and P. The effect of biochars on soil properties, including available nutrients, soil moisture, soil OC, pH and EC were evaluated at the end of the growth period.

The final chapter (Chapter 5) integrates the research findings of the specific studies and draws conclusions and makes practical recommendations based on the results. Also included in this thesis are two Appendices. Appendix A consists of additional supplemental data from growth chamber experiments, while Appendix B includes some supplemental data from the field study.

2. LITERATURE REVIEW

2.1 Introduction

Biochar is a carbon (C) rich, largely stable and refractory organic C compound that is produced when biomass from different sources is combusted in presence of limited or without oxygen (O_2) (Verheijen et al., 2010). The term biochar originated in around 1998 for the residual of biomass pyrolysis (Bapat and Manahan, 1998). Soil amendment with biochar began to attract extensive attention in the late 1980's because of its potential for C sequestration in soils (Kuhlbusch and Crutzen, 1995; Kwapinski et al., 2010). This alteration of use has prompted a paradigm shift in referring to BC instead as "Biochar" for C sequestration purposes (Lehman, 2007; Laird, 2008; Spokas et al., 2012; Wayne, 2012).

Biomass is the worlds largest and the most sustainable energy resource. According to the estimation of Torres et al. (2007), approximately 220 billion dry tonnes of annual available biomass are produced in the world. Production of renewable energy and by-products from non-food biomass is a sustainable strategy to address the worldwide energy and climate change challenges (Demirbas, 2001). Different non-food biomass resulting from plants and animals is being explored as a feedstock for biochar, biofuels and industrial chemicals. Biomass is a mixture of hemicellulose, cellulose, lignin and minor amounts of other organics which is pyrolyse or degrade at different rates and by different mechanisms and pathways (Azargohara et al., 2013). Pyrolysis is combustion under low or zero O_2 condition. The rate and extent of decomposition of each of these components depends on the process parameters of the reactor (pyrolysis), including temperature, biomass heating rate and pressure (Bridgwater et al., 1999). These production parameters along with feedstock types and storage conditions determine the physical and chemical qualities of the produced biochar as a soil amendment (Antal and Gronli, 2003.). Commonly measured quality parameters of biochar include bulk density, organic carbon (OC) content, ash content, nutrient content, overall elemental composition, surface area,

porosity, surface functional groups, cation exchange capacity (CEC), iodine number, and sorption properties (Gaskin et al., 2009). In pyrolysis of biochar, most of the calcium (Ca), magnesium (Mg), potassium (K), phosphorus (P), and plant micronutrients, and about half of the nitrogen (N) and sulpfur (S) in the biomass feedstock are partitioned into the biochar fraction (Laird et al., 2010). As a result use of the biochar as a soil amendment returns most of the nutrients back to the soils. Biochar also increases the capacity of soils to adsorb plant nutrients (Lehman et al., 2007; Cheng et al., 2008; Spokas et al., 2012) thereby reducing leaching losses of nutrients.

Many studies reported that biochar application to a soil significantly improved soil qualities and increased crop yield (Lehman, 2006; Chan et al., 2010; and Spokas et al., 2012). Much of the research has been done on highly weathered Oxisols and Ultisols of the tropics and some from the temperate and arid regions. The different impacts of biochar on soil properties needed to be well understood along with how biochar form and function respond to production conditions and feedstock sources, and include agronomic responses in a variety experiments. This literature review attempts to consolidate and summarize the current knowledge surrounding biochar production, along with its properties and impacts on soil and plants when used as a soil amendment.

2.2 Biomass feedstock

The response of soils and plants to biochar amendment cannot be properly discussed and understood without first describing the biomass feedstock, because feedstock quality largely affects the biochar properties, which thus affect the agronomic yield. Biomass feedstocks used for biochar production influence biochar characteristics, including nutrient constituents, liming characteristics, density, porosity, and hardness (Spokas et al., 2012). The term “biomass” refers to the total mass of living matter in forestry, purpose-grown agricultural crops, trees and plants, animal wastes and manures, and organic, agricultural, agro-industrial, and domestic wastes (Demirbas, 2002). Such materials can be used as a source of energy (Hassan et al., 2012; YukselI et al., 2011) and are available on a renewable basis as a result of plant growth (Bridgwater et al., 1999) or indirectly available as a by-product of human and animal activities (i.e. organic wastes). Renewable biomass forms can be used directly to produce alternative energy by converting into any other type of value-added product such as biodiesel, bio-fuel, (Enweremadu and Mbarawa,

2009; Börjesson and Berglund, 2006; Chung et al., 2009); sysngas and biochar (Bridgewater, 1999, Laird, 2008, Lehman, 2007, Spokas et al., 2012).

2.2.1 Biomass composition and pyrolysis behavior

Plant biomass has a complex composition, and is mainly comprised of hemicellulose, cellulose, lignin, along with smaller quantities of organic extractives (tannins, fatty acids, resins), and inorganic minerals. Cellulose is an organic compound made of very long unbranched fibrils (Updegraff, 1969; O'Sulivan, 1997).

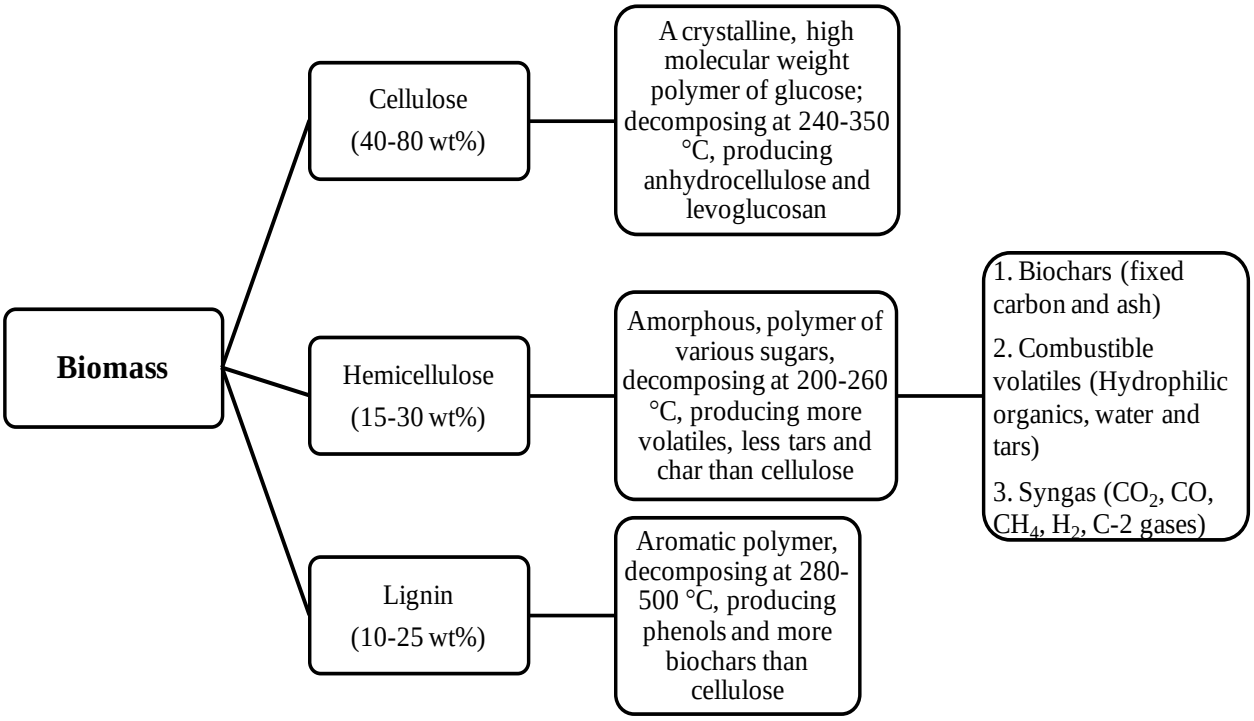

Fig. 2.1. Biomass structure, composition, thermal decomposition characteristics and final products of pyrolysis (Compiled from Mok and Antal, 1983; Yang et al., 2012; Yin, 2012)

Hemicellulose consists of several heteropolymers commonly known as matrix polysaccharides, such as arabinoxylans, present along with cellulose in almost all plant cell walls. They have a random, amorphous structure with little strength. Cellulose is crystalline, strong, and resistant to hydrolysis, while hemicellulose has a random, amorphous structure with little strength. Lignin, which is based on a phenylpropane polymer, is the largest

noncarbohydrate fraction of lignocelluloses (Sjostrom, 1993) and has an amorphous structure. Unlike cellulose, lignin cannot be depolymerised to its original monomers. Cellulose, hemicellulose, and lignin, the principal constituents of biomass, have distinctive thermal decomposition behaviors (Fig. 2.1) and have different reaction kinetics which depends on the heating rate in the thermodynamic conversion process. Hemicellulose is the most reactive constituent (Probstein and Hicks, 1982). The reaction rates, products, and other thermal behavior of biomass pyrolysis are considered a combination of the behavior of these constituents of biomass as shown in Fig. 2.1.

2.2.1.1 Cellulose pyrolysis

Cellulose is the major component of most biomass (40-80 wt %) and is the major source of the combustible volatiles that fuel flaming combustion. Numerous studies of pyrolytic thermal degradation of cellulose under various conditions have been reported and a simplified, two-pathway mechanism of its decomposition has been generally accepted (Fig. 2.2).

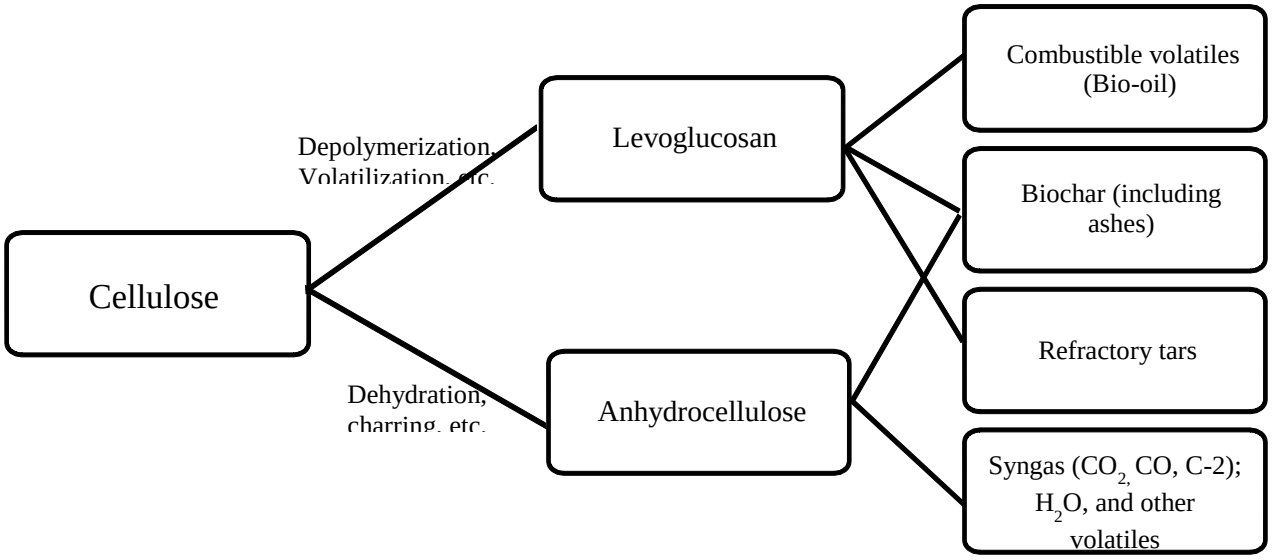

Fig. 2.2. Thermal degradation reaction pathway of cellulose and the main products (Compiled from Arseneau, 1971; Mok and Antal, 1983; Yang et al., 2007; Yin, 2012)

The depolymerisation and volatilization reactions occur at high temperatures, while the dehydration and charring occurs at relatively low temperatures and the transition is found to occur at around 300 °C (Yang et al., 2007; Yin, 2012). The first pathway occurs below 300 °C,

in which reduction of molecular weight, the appearance of free radicals, oxidation, dehydration, decarboxylation, and decarbonylation chemical reactions may occur. The intermediate product is anhydrocellulose, and final products are mainly CO, CO_2, H_2O, and a biochar residue. The second pathway occurs at temperatures above 300 °C and involves decomposition of cellulose to tarry pyrolyzate-containing intermediate component levoglucosan (22-50 %), which then vaporizes and decomposes with increasing temperature. When the temperature is increased above 300 °C, the amount of tarry products increases while the proportion of biochar component reduces and the yield of levoglucosan remain constant. The final pyrolysis products of cellulose under 500 °C are biochar, refractory tar (mainly levoglucosan), water, CO_2 and CO (Mok and Antal, 1983; Funakuzuri et al., 1986; Yin, 2012). The yield of light hydrocarbons, i.e., C1-C4, is negligible below 500 °C but becomes considerable at high temperatures (Scott et al., 1988) and is mostly C-2 gases (Mok and Antal, 1983). Tar yield, which is mostly phenolic compounds, begins to drop as the pyrolysis temperature is raised above 600 °C (Hajaligol et al., 1982) and pyrolysis of cellulose is essentially complete above 600 °C (Funazukuri et al., 1986).

2.2.1.2 Hemicellulose pyrolysis

Hemicellulose is the component of biomass (15–30 wt %) in which xylans are the most important hemicelluloses of hardwoods and most crop plants (Scheller and Ulvskov, 2010). Hemicelluloses are the most reactive major component of biomass decomposing in the temperature range 200-260 °C (Koufopanos et al., 1989; Yin, 2012). Soltes and Elder (1981) first proposed a two step process of hemicelluloses thermal decomposition. First, the polymer is broken down into water soluble fragments and conversion to monomeric units, and finally decomposition of these monomeric units into different volatiles. Hemicelluloses produce more gases, less tar and biochar than cellulose, and no levoglucosan (Yin, 2012). It also produces more methanol and acetic acid in thermal decomposition than cellulose.

2.2.1.3 Lignin pyrolysis

Lignin, the third major component of woody biomass (10-25 wt %), serves as cement between the wood fibers and as a stiffening agent within them, and is the least reactive component of biomass. Usually a relatively higher temperature (280-500 °C) is necessary for the thermal decomposition of most lignin (Yin, 2012), although some physical and/or chemical

changes (e.g., depolymerization, loss of methanol) may occur at lower temperatures (Koufopanos et al., 1989). Pyrolysis of lignin yields more biochar and tar than cellulose, including phenols. Soltes and Elder (1981) have reported a product composition of 51-66 % biochar, 14-15 % tar, 13-28 % pyroligneous acid and about 12 % gaseous products (consisting mainly of CO, CH_4 and C_2H_6). It has been observed that biochar from lignin tends to have a lower hydrogen content (Schuhmacher et al. 1960; Michels and Landais. 1994) and biochar from cellulose tends to achieve a higher C content (Yokokawa et al., 1964).

2.2.2 Classification of biomass feedstock

There is no established way of categorizing biomass in the literature. However, based on biomass sources, biomass can be grossly classified into four categories: forest resources, agricultural resources, animal resources and municipal solid waste resources (Table 2.1). Each of the individual categories can be further classified as intact or residual sources. Agricultural residues such as straws, husks, nut shells, fruit shells, plant stalks, stovers, green leaves, and molasses are potential feedstocks for biochar production. However, the choice of thermodynamic conversion processes depends largely upon the biomass moisture content (McKendry, 2002) and biomass sources. High moisture content biomass, such as sugarcane (*Saccharum officinarum*), requires a 'wet' conversion process, involving hydrothermal carbonization, whereas a 'dry' biomass such as wood chips is more economically suited to fast or gasification pyrolysis. There is a need to utilize biomass resources efficiently in future. Agricultural wastes such as rice or coconut husks have been used in developing countries for small-scale power and heat production (Hashim and Ho, 2011) for a long time.

Biomass resources are categorized broadly into four major divisions and all of these sources can potentially be used for energy and biochar production using suitable thermal conversion processes (Table 2.1). Ligno-cellulosic feedstocks including intact resources and residues such as willow (Kwapinski et al., 2010), eucalyptus (Petter et al., 2012; Kimetu et al., 2008; Namgay et al., 2010) pine wood (Kwapinski et al., 2010), olive pruning (Alburquerque et al., 2013), rice straw (Weixiang et al., 2012), rice husk (Carter et al., 2013, Haefele et al., 2011); wheat straw (Alburquerque et al., 2013; Zhang et al., 2010), and waste tea (Uzun et al., 2010) have shown high potentials as feedstock materials for the pyrolysis process. Feedstocks including animal resources and wastes such as poultry litter (Chang et al., 2010; Rajkovich et al.,

2012; Widowati et al., 2012), chicken manure (Togo et al., 2008), and cattle manures (Uzoma et al., 2011; Rajkovich et al., 2012) are already recognized as a source of good quality nutrient-rich biochar. The organic portion of municipal solid waste can also be important source (Dukua et al., 2011) for nutrient-rich biochar production.

Table 2.1. Biomass resources classification for biochar production

Category	Sources	Descriptions
Forest resources	Intact forest sources	Any type of wood. For example pine, willow, popler, eucalytus, aspen, bamboo, etc.
	Residual forest sources	Sawdust, shavings from pulp mills and sawmills, barks, branches, wood chips, left over tree tops, and leaves from harvest and thinning operations, stumps.
Agricultural resources	Intact agricultural sources	Switch grasses, weeds, forage grasses and hay etc.
	Agricultural residues and waste sources	All kinds of residues (straw, chaff and hull) from crops (rice, wheat, barley, corn, clover, canola, palm-oil, soybean, flax, oat, sugarcane, coffee etc.)
Animal resources	Animal residues and waste sources	Livestock manures and bedding, poultry litters, livestock carcass, slaughterhouse meat and bone waste.
Municipal solid waste(MSW) resources	Residential sources	Kitchen waste
	Non-residential sources	All kinds of industrial and municipal organic wastes.

2.2.3 Biomass feedstock and biochar quality

The feedstock biomass material used for biochar production has a strong influence on the initial biochar characteristics (Gaskin et al., 2008). According to Zimmerman (2010), biomass feedstock and pyrolysis conditions (reactor temperatures) seem to be most important as shown in a two-year incubation study. In particular, the pyrolysis peak temperature, particle residence time

and heating rate are most important to influence the biochar quality (Brown, 2009). The most important factors determining the quality of biochar are type of biomass used as feedstock (Gaskin et al., 2008) and thermodynamic process conditions. Both energy conversion efficiency and the quality of the bio-oil, biochar and syn-gas co-products are dependent on the nature of the biomass feedstock. The inherent properties of the biomass determine both the choice of conversion process and the quality of the produced products. Depending on the thermodynamic conversion process selected, particular biomass feedstock properties become important during subsequent processing. The main feedstock properties of interest, during subsequent processing as an biochar source, relate to: moisture content (intrinsic and extrinsic), calorific value, proportions of fixed C and volatiles, ash/residue content, alkali metal content, and cellulose/lignin ratio.

Feedstock rich in cellulose produce bio-oil rich in pyrolytic sugars, biochar along with considerable amount of tar, whereas feedstocks high in lignin produce more biochar than bio-oil and tar (Soltes and Elder, 1981). The higher moisture (>10 % moisture by mass) content of the feedstock usually adversely affect the overall energy balance for the conversion process (McKendry, 2002) as it takes energy to simply get rid of the water. Therefore, in order to reduce energy loss, pyrolysis reactors should be fed materials with low moisture content. The biomass calorific value determines the energy content, or heat value. As the moisture content of biomass increases, the calorific value usually decreases, which ultimately affects the feedstock as well as biochar quality.

Biomass stores renewable energy from sunlight via the process of photosynthesis. Upon pyrolysis of biomass, this chemical energy stored in biochar into two forms: fixed C and volatiles. The solid content and the fixed C content, is the mass remaining after the release of volatiles, without the ash and moisture. The volatile matter and fixed C contents of biomass provide a measure of choosing to pyrolysis process in which biomass can be thermally decomposed and subsequently gasified, or oxidised, depending on how the biomass is to be utilized as an energy source. The lower the O: C and H: C ratios in the biomass feedstock, the higher the stability of biochar in soils (McKendry, 2002). The thermodynamic decomposition of a biomass in the presence of O_2 produces a solid residue called ash. The alkali metal content of biomass (i.e. Na, K, Mg and Ca) is especially important for any thermo-chemical conversion processes. The reaction of alkali metals with silica present in the ash produces a sticky, mobile

liquid phase, which may lead to operational difficulties. (McKendry, 2002). The decomposition rate between biomass varies and usually required different production temperatures. The moisture contents and particle sizes of feedstock are important as wet feedstocks with large particle sizes will require more heat energy for pyrolysis, which is increases production costs.

2.3 Biochar production technologies

The conversion of biomass into energy (e.g. syn-gas, bio-oil or biochar) through a thermodynamic decomposition process is not a new concept. Humankind has used pyrolysis and related processes for thousands of years. The earliest known examples are the use of charcoal, produced as residue from cooking fires, for cave drawings by Cro-Magnon man (circa 38,000 years ago) (Antal and Grønli, 2003). There is evidence that the Bronze Age people intentionally produced charcoal to smelt various types of metals. For thousands of years charcoal has been a preferred cooking fuel in eastern Asia and China. The pyrolysis process is also reported to date back to ancient Egyptian times, to produce tar for caulking boats and producing certain embalming agents (UNH Bio-oil Team Report, 2002). Pyrolysis was the primary source of many organic compounds for industrial and medicinal uses, prior to the invention of petro energy; and some high value liquid products, such as flavourings, are still produced by wood pyrolysis (Bridgwater and Peacocke, 2000). In the 1980s, researchers found that the pyrolysis liquid yield could be increased using fast pyrolysis where a biomass feedstock is heated at a rapid rate and the vapors produced are also condensed rapidly (Mohan et al., 2006). Since Victorian times, pyrolysis (low O_2) and gasification (high O_2) combustion processes have been used to extract liquid as a synthetic crude oil from coal. It is only more recently that biomass and organic wastes have become a feedstock for thermodynamical decomposition processes (Mistry et al, 2008). Since then, pyrolysis processes have been enhanced and are now widely used in biocharcoal, bio-oil and syn-gas production.

2.3.1 Pyrolysis technology and processes

Pyrolysis is the breaking down (i.e., lysis) of a material using heat (i.e., pyro) (Fig. 2.3). Pyrolysis specifically refers to decomposition of biomass at elevated temperatures in the absence of O_2 or in a depleted O_2 environment (Bridgwater, 1994). It involves the simultaneous change of chemical composition and physical phase, and is an irreversible process. A pyrolysis process

proceeds in three steps (Demirbas, 2006). In the initial step, there is moisture and some volatile loss (Equation 1). Primary biochar occurs in the secondary step (Equation 2). In step two, breakdown of cellulose and hemicelluloses takes place and CO and CO_2 are emitted. Exothermic reactions cause biomass temperature to rise depending upon feedstock, reactant temperature and reactor conditions; emission of CH_4, H_2, and C_2H_2 is also evident in this stage. During the third stage, the biochar decomposes at a very slow rate and a C-rich residual solid forms. The formation of secondary charring (Equation 3) makes the biochar less reactive. An external energy required to continue the process and usually complete the decomposition process.

$$Biomass = Water + Unreacted\ solid\ residues \ldots\ldots\ldots (Equation\ 1)$$

$$Unreacted\ solid\ residue = (Volatile + Gases)_1 + (Biochar)_1 \ldots\ldots\ldots (Equation\ 2)$$

$$Biochar_1 = (Volatile + Gases)_2 + (Biochar)_2 \ldots\ldots\ldots (Equation\ 3)$$

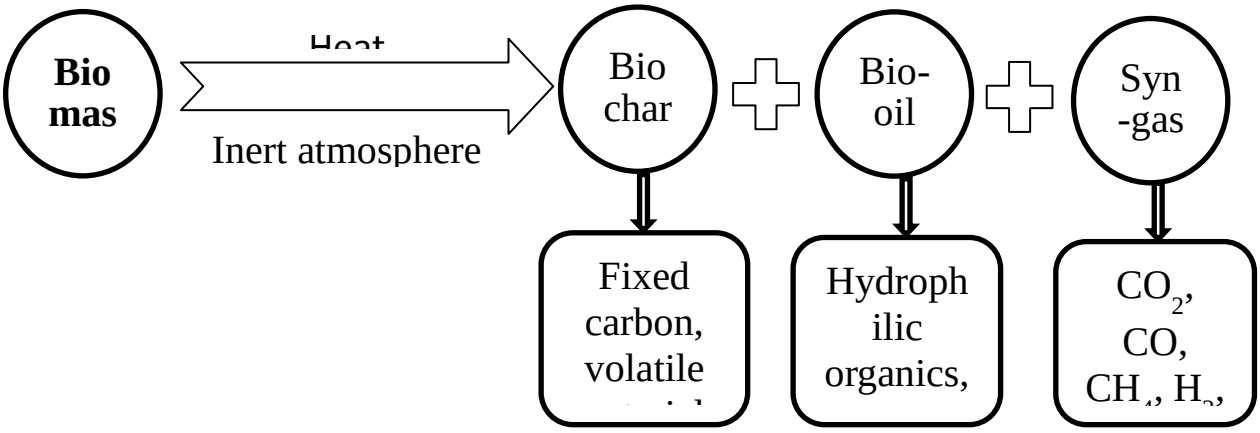

Fig. 2.3. Simplified representation of biomass pyrolysis process and products

Various production techniques, product composition and impacts on the product yields are reported in the Table 2.2. Product composition from these thermodynamic processes varies with reaction conditions and includes noncondensable gases (synthetic or producer gas), condensable vapors/liquids (bio-oil, tar), and solids (biochar, ash) (Gaunt and Lehmann, 2008; Brewer et al., 2009; Spokas et al., 2012). A range of process conditions, such as the composition of the feedstock, temperature and heating rate can be optimized to provide different amounts and properties of products. Volatile products can be captured to provide energy, or upgraded to specific chemical products (e.g. wood preservative, meat browning, food flavoring, adhesives, etc.) (Czernik and Bridgwater, 2004; Lehmann, 2007a). Depending on the operational processes,

time and temperature, the thermochemical technologies for transforming biomass into renewable energy products can be classified into slow pyrolysis, fast pyrolysis, flash pyrolysis, gasification, torrefaction, hydrothermal carbonization, and microwave assisted pyrolysis. Again depending on the temperature of the reactants pyrolysis can be an endothermic process which requires high temperature or exothermic as the reaction temperature decreases (Mok and Antal, 1983). The modern day biochar production is primarily focused on advanced pyrolysis process (Lima et al., 2010; Lima and Marshall 2010; Spokas et al., 2012). However, the traditional charcoal production system is still in use (Major et al., 2010; Spokas et al., 2012). The advanced pyrolysis system allows precise control of operating conditions, which, coupled with feedstock selection, can regulate the physical, chemical properties of biochar.

2.3.1.1 Slow pyrolysis

Slow pyrolysis is characterized by slow heating (i.e., minnutes to hours) of the organic material to 400 °C in the absence of O_2 and relatively long residence times (Mohan et al., 2006). Modern slow pyrolysis often takes place in continuous reactors (e.g., drum pyrolysers, rotary kilns, or screw pyrolysers; Brown, 2009). Slow pyrolyzers are either batch systems known as 'charcoal kilns', or continuous systems that slowly heat the biomass to >400 °C in the absence of O_2. Moisture content and particle size are not critical for the charcoal kilns while continuous systems do specify some size reduction and drying for optimal results. Product yields from slow pyrolysis are approximately 35 % biochar, 30 % bio-oil, and 35 % syn-gas by mass. The product biochar in which C is distributed in less polycondensed aromatic structures, and has relatively higher O: C ratios, greater recovery of C, N, and S and better contribution to soil fertility (Laird et al., 2009; Brewer et al., 2009; Yin et al., 2012).

2.3.1.2 Fast pyrolysis

Fast pyrolysis is a thermochemical conversion process characterized by rapid heating of biomass feedstock in an O_2 free condition under moderate temperature levels (e.g., 500 °C) and with rapid quenching of the intermediate volatile products. Fast pyrolysis is one of the attractive technologies for liquid biofuels production (Bridgwater and Peacocke, 2000; Boateng et al., 2008; Vamvuka, 2011). Dried biomass feedstock is cut into pieces, blown into a hot reactor, and exposed to heat transfer for just a few milliseconds to seconds (Bridgwater et al., 2007; Laird et

al., 2009). In fast pyrolysis, the thermal decomposition process occurs in an inert atmosphere using high heating rates and short residence times (>2s to <1 min) at about 450-550 °C to maximize liquid production with solid char and non-condensable gas as low yield co-products (Bridgwater, 1999; Garcia-Perez et al., 2008). A number of fast pyrolysis technologies exist, such as fluidized bed systems, systems using ablative reactors, and systems using pyrolysis centrifuge reactors (Bridgwater et al., 1999; Bech et al., 2009). The heating rates used in pyrolysis experiments vary considerably in the literature, however, the boundary between 'slow' and 'fast' is somewhat arbitrary. It is found in many studies only slow or fast pyrolysis is indicated without giving any specific heating rate value. However, Neves et al., (2011) suggested that a heating rate threshold of 10 °C s^{-1} can be adopted to classify into slow or fast pyrolysis. In fast pyrolysis, the product biochar has C that is distributed in more polycondensed aromatic structures that are resistant to microbial degradation, and therefore better for C sequestration. Fast pyrolysis biochar also have higher surface areas (>400 m^2 g^{-1}) and relatively lower content of C, N, and S; and greater P and base cation content (Bridgewater, 2006; Brewer et al., 2009; Laird et al., 2009; Spokas et al., 2012; Yin et al., 2012).

2.3.2. Effect of production technology and process on biochar production and quality

The composition of actual biochar products is noted to be variable as reported in the literature and largely depends on type of biomass feedstocks, production conditions and technology. For biochar yields, low operational temperatures and low heating rates give maximum yields of biochar (Demirbas, 2008). Generally, increasing the pyrolysis temperature reduces the char yield and increases the gas yield (Domínguez et al., 2007; Domínguez et al., 2008). Long residence times of volatiles in reactor and high temperatures decrease tar production but increase char formation as a result of the extension of secondary reactions (Fernández et al., 2009). Higher heating rates favour a quick release of volatiles, modifying the solid residue structure with an increased yield of the liquid and gaseous fractions (Menéndez et al., 2007). Other variables that have to be considered in a pyrolysis process are the reactor type (Bridgewater, 2003), sample size (Tsai et al., 2007), and pressure (Cetin et al., 2005), all of which might also alter the final product distribution.

The biochar quality (both physical and chemical properties) also depend on the pyrolysis conditions such as final pyrolysis temperature, rate of heating, residence time and the type and

composition of the biomass feedstock (Shafidazeh, 1982; Wildman and Derbyshire, 1991; Laird, 2008; Mukherjee et al., 2011; Zimmerman et al., 2011; Spokas et al., 2012). Slow and fast pyrolysis results in biochars with different physicochemical qualities thus providing different effects in the soil environment upon application (Brewer et al., 2009; Brown, 2009). For example, biochars produced under high-temperature pyrolysis (>550 °C) are highly aromatic and recalcitrant in nature (Singh and Cowie, 2008), and generally have high surface areas (>400 $m^2 g^{-1}$) (Downie et al. 2009; Keiluweit et al. 2010), and act as a good adsorbents (Mizuta et al., 2004; Lima and Marshall, 2005). The active surface area is enhanced by high temperature conditions, while CEC is decreased as a result of loss of functional groups (Gou and Rockstraw, 2007). Studies have indicated that high temperatures can result in nutrient loss via volatilization (Olsson et al., 1997; Jensen et al., 2000). When the temperature exceeds 500 °C, as in most cases of fast, flash, and gasification processes, as much as 50 % of N may be lost (Gaskin et al., 2008). In addition, P concentration was found to be decreased at higher temperatures. On the other hand, biochars from low-temperature pyrolysis (<550 °C), have less condensed C structure, and have higher concentration of nutrients (e.g. N, S) that are increasingly lost at higher temperatures (Keiluweit et al. 2010) and low surface area (Lehmann and Joseph, 2009). The biochars produced at lower temperatures are expected to have a greater reactivity in soils and a better contribution to soil fertility (Steinbeiss et al. 2009). For biochar production, slow pyrolysis is currently seen as the preferred technology as it maximizes biochar yield over production of bioenergy (Lehmann and Joseph, 2009; Sohi et al., 2010).

In a study on biochar characterization, Brewer et al. (2009) found that chars from fast pyrolysis and gasification are physically and chemically different from traditional hardwood charcoals and chars prepared from herbaceous feedstocks by slow pyrolysis. The types of C present appear to depend on process temperature and, to a lesser extent, reaction time. However, biochar produced from gasification is reported to carry the risk of higher levels of metals and minerals that may be concentrated in to biochar, with potential safety implications with regard to application to soil (Fernandes and Brooks, 2003).

Table 2.2. Processes of thermochemical decomposition of Organic feedstocks, conversion characteristics and the product composition

Pyrolysis process	**Reactor temperature**	**Residency time**	**Heating rate**	**Product yields (% dry feedstock mass)**			**Proximate analysis (%) (Dry weight basis)**				**Pyrolysis product stream**	**References**
			°C s^{-1}	Biochar	Bio-oil	Syn-gas	H_2O	VM	Ash	Fixed C		
Slow Pyrolysis	Low temperature pyrolysis (350 - 500 °C)	hrs	1-100	20-35	15-30	10-35	0-5	5-20	2-10	40-90	Use for commercial biochar production	Laird et al., 2009; Brewer et al., 2009; Yin et al., 2012.
Fast Pyrolysis	High temperature pyrolysis (450 - 600 °C)	>2s -<1 min	726-9726	10-30	50-70	5-20	0-5	40	30	40-60	Use for commercial bio-oil and biochar production	Laird et al., 2009; Yin et al., 2012, Bridgewater, 2006;
Flash	High temperature pyrolysis (8000-1100 °C)	< 2 s	700-9000	15-25	60-80	10-20	0-5	5-26	0-40	40-60	To process biomass, decompose waste, produce bio-oil and charcoal	Laird et al., 2009; Amutio et al., 2012; Bridgwater, 2012; Neves et al., 2011; Mohan et al., 2006
Gasification	Very high temperatures (>800 °C),	s to mins	Variable	5-10	0-10	80–95	n/a	n/a	n/a	n/a	Production of synthetic gas (CO, H_2 and CO_2)	Laird et al., 2009; Brewer et al., 2009; Yin et al., 2012

Table 2.2. Continued

Thermal decomposition process	Reactor temperature	Residency time	Heating rate	Typical product yields (% dry feedstock mass)			Proximate analysis (%) (Dry weight basis)				Pyrolysis product streams	References
			°C s^{-1}	Biochar	Bio-oil	Syn-gas	H_2O	VM	Ash	Fixed C		
Torrefaction	Mild form of pyrolysis at temperatures 200-320 °C	hrs	<1	40-90	0	10-60	0-1	50-85	2-10	13-38	Fuel upgrading of woody biomass and biochar production	Spokas et al., 2012
Hydrothermal carbonization	Wet pyrolysis at temperature (180-200 °C) and stream pressure	mins to hrs	n/a†	n/a	n/a	n/a	10-40	50-90	5-15	4-10	To produce biocoal (100% C) powder, can be use as soil amendment	Funke and Ziegler, 2010
Microwave assisted pyrolysis	Moderate temperatures (300-500 °C)	mins to hrs	n/a	n/a	n/a	n/a	10-25	20-30	20-25	50-60	To produce fuel gases, bio-oil and biochar	Yin et al., 2012; Laque et al., 2012

† Not available (n/a).

2.4 Biochar as a soil amendment

Biochar application to soils is reported to create a "win-win" situation by sequestering C, while at the same time improving soil properties and functions and increasing agronomic yield (Lehmann and Joseph, 2009; Woolf et al., 2010; Spokas et al., 2012). Biochar has been recognized as a possible means to improve soil fertility as well as other ecosystem services and C sequestration (Lehmann et al., 2006; Lehman, 2007a; Lehmann, 2007b; Laird, 2008; Sohi et al., 2010).

It is important to understand how biochar properties specifically influence soil properties. The biochar qualities (both physical and chemical properties) depend on the pyrolysis conditions and sources of feedstock as covered into previous sections. In addition, biochar properties can change over time in soil and these changes may also be affected by the initial properties of the biochars (Joseph et al., 2010). It is evident from the literature that animal sources of biochar such as manures have greater nutrient supply ability (Chan et al., 2007; Spokas et al., 2012) over agricultural or forest biomass sources biochar (Table 2.3). While it may enhance nutrient supply to plants and soil microorganisms, biochar may primarily serve as a catalyst that enhances plant uptake of nutrients and water. Besides the abilities of biochar to retain and supply nutrients, effects on soil fertility have also been explained mainly by a pH increase in acid soils (Van Zwieten et al., 2010a) or improved nutrient retention through cation adsorption (Liang et al., 2006) via its large surface area. Biochar has also been shown to influence a range of soil chemical properties related to nutrient availability, including CEC and EC, and is revealed to have different environmental impacts in different climates (Ippolito et al., 2012a).

2.4.1 Effect of different biomass feedstock on biochar nutrient content

The nutrient concentration of biochar varies with the feedstock resources used for production (Table 2.3). Amending soils with biochar from various feedstocks at the same rate will therefore add different amounts of C and nutrients that can subsequently affect plant growth. Feedstock from animal sources (e.g., poultry and cattle manure) produce biochar with high pH and P content, relatively high P and less cation content of the feedstock manure and lower C: N ratio. Wood source can result in biochar with very high C: N ratio and very low P concentrations having close to neutral pH (Table 2.3). Gaskin (2010) compared biochar derived from peanut

shells or wood chips in an Ultisols in the southeastern United States and found peanut-shell biochar had higher nutrient concentrations and raised the pH and base cation concentrations when added to the soil, while wood-chip derived biochar had little effect on these parameters.

2.4.2 Soil properties and biochar

2.4.2.1 Porosity and bulk density

Numerous soil benefits have been reported associated with the physical properties of biochar. Biochar incorporation can alter soil physical properties such as structure, pore size distribution and density, with implications for soil aeration, water holding capacity, plant growth, and soil workability (Downie et al., 2009). A wide ranges of pore sizes within the biochar arising from retaining the cell wall structure of the biomass feedstock results in a large surface area and a low bulk density. Evidence suggests that biochar application may improve soil aeration, particularly in fine-textured soils (Kolb, 2009). Biochar has a bulk density much lower than that of mineral soils (~0.3 Mg m^{-3} for biochar compared to typical soil bulk density of 1.39 Mg m^{-3}); therefore, application of large amounts of biochar can reduce the overall total bulk density of the soil (Brady and Weil, 2004).

2.4.2.2 Surface area and soil moisture retention

Biochar addition is reported to increase soil moisture retention which is an indirect result of alterations in soil aggregation and structure after biochar application (Brodowski et al., 2006). Water retention of soil is determined by the distribution and connectivity of pores in the soil matrix, which is largely affected by soil texture, aggregation, and SOM content (Brady and Weil, 2004). Kishimoto and Sugiura (1985) estimated the inner surface area of charcoal formed between 400 and 1000 °C to range from 200 to 400 m^2 g^{-1}. Van Zwieten et al. (2009) reported the surface area of biochar derived from papermill waste with slow pyrolysis to be 115 m^2 g^{-1}. These properties are expected to change over time with physical weathering, but have not been explicitly examined, resulting in uncertainties associated with the longevity of these beneficial physical changes in soil. Glaser et al. (2002) reported that Anthrosols enriched with charcoal had

Table 2.3. Chemical composition of biochar products from different feedstocks

Feedstocks	**Pyrolysis** (temp °C)	**C**† (%)	**N**† (%)	**C: N** (ratio)	**Total P** (mg kg^{-1})	**pH** (H_20)	**VM**† (%)	**SSA (N_2)**‡ (m^2 g^{-1})	**CEC** (cmol kg^{-1})	**O: C** (molar ratio)	**References**
Agricultural biomass sources											
Corn	300	59. 5	1.2	51	1369	7.3	51.9	4.7	70.8	n/a§	Rajkovich et al., 2012
Corn cob	300	70.5	0.8	87	n/a	n/a	n/a	2.4	n/a	0.20	Zheng et al., 2010
Corn stover	350	60.4	1.2	51	1889	9.4	48.8	293.0	41.9	0.29	Lehmann et al., 2011
Wheat straw	370	62.8	0.8	79	800	11.0	n/a	n/a	47.0	n/a	Alburquerque et al., 2013
Peanut hull	400	74.8	2.7	28	2600	7.9	38.4	0.5	13.6	0.01	Novak et al., 2009
Dried distillers grain	400	69.4	7.4	9	n/a	n/a	37.6	0.3	n/a	0.09	Spokas et al., 2010
Corn	400	62.6	1.1	58	n/a	9.2	44.7	3.9	79.6	n/a	Rajkovich et al., 2012
Switchgrass	500	84.4	1.1	79	2400	8.0	13.4	62.2	8.2	0.04	Novak et al., 2009b
Corn cob	550	82.6	0.8	98	n/a	n/a	n/a	30.6	n/a	0.07	Zheng et al., 2010
Corn stover	600	70.6	1.1	66	2114	9.4	23.5	527.0	25.2	0.10	Lehmann et al., 2011
Sugarcane bagasse	600	63.2	0.4	171	0.8	7.3	n/a	32.9	n/a	n/a	Chen et al., 2010
Switchgrass	824	25.4	0.3	85	n/a	n/a	7.5	46.1	n/a	0.18	Brewer et al., 2011
Wood (Forestry) sources											
Hazelnut	300	69.9	0.5	159	397	6.4	48.8	1.3	5.9	n/a	Rajkovich et al., 2012
Oak	300	63.9	0.1	520	6	4.3	61.1	n/a	41.4	n/a	Rajkovich et al., 2012
Oak wood	350	74.9	0.2	455	12	4.8	60.8	450.0	29.4	0.20	Lehmann et al., 2011
Mixed hardwood	400	79.2	0.5	158	n/a	n/a	16.8	8.1	n/a	0.14	Brewer et al., 2011

† Carbon (C), Nitrogen (N) and Volatile Matter (VM) expressed on a dry weight basis
‡ Specific surface area measured based on Brunauer–Emmett–Teller (BET) –N_2 adsorption
§ Not available (n/a)

Table 2.3. Continued

Feedstocks	Pyrolysis (temp °C)	C† (%)	N† (%)	C: N (ratio)	Total P (mg kg^{-1})	pH (H_20)	VM† (%)	SSA (N_2)‡ (m^2 g^{-1})	CEC (cmol kg^{-1})	O: C (molar ratio)	References
Wood (Forestry) sources											
Hazelnut	400	75.8	0.5	158	298	7.7	43.5	1.6	10.2	n/a§	Rajkovich et al., 2012
Pine	400	74.4	0.1	827	35	4.6	45.5	1.4	30.4	n/a	Rajkovich et al., 2012
Eastern hemlock	550	75.7	0.3	252	n/a	n/a	27.1	5.8	n/a	0.20	Brewer et al., 2011
Eucalyptus wood	550	47.9	0.0	1597	217	8.8	n/a	n/a	91.2	n/a	Singh et al., 2010b
Oak wood	600	87.5	0.2	489	29	6.4	27.5	642.0	7.6	0.07	Lehmann et al., 2011
Bamboo	600	68.1	0.9	78	680	8.2	n/a	330.0	n/a	n/a	Ding et al., 2010
Animal sources											
Poultry manure	300	25.9	2.2	12	26414	8.1	46.8	1.2	36.2	n/a	Rajkovich et al., 2012
Dairy manure	300	56.1	2.7	21	5391	8.9	50.5	n/a	44.4	n/a	Rajkovich et al., 2012
Poultry litter	350	29.3	2.0	15	21,256	9.7	47.2	47.0	12.1	0.41	Lehmann et al., 2011
poultry litter	350	46.1	4.9	9	29400	8.7	36.7	1.1	1.1	0.14	Novak et al., 2009b
Poultry manure	400	39.3	6.1	6	5763	9.2	n/a	n/a	14.5	n/a	Singh et al., 2010b
Cow manure	400	20.0	2.0	10	4359	9.0	n/a	n/a	22.2	n/a	Singh et al., 2010b
Dairy manure	500	59.4	2.6	23	18505	9.4	42.7	n/a	47.8	n/a	Rajkovich et al., 2012
Poultry litter	600	23.6	0.9	25	23,596	10.3	44.1	94.0	5.9	0.62	Lehmann et al., 2011
Poultry manure	600	23.6	0.9	28	23,596	10.7	44.2	6.7	5.9	n/a	Rajkovich et al., 2012
Poultry litter	700	44.0	2.8	16	42800	10.3	14.1	9.0	n/a	<0.01	Novak et al., 2009b

† Carbon (C), Nitrogen (N) and Volatile Matter (VM) expressed on a dry weight basis
‡ Specific surface area measured based on Brunauer–Emmett–Teller (BET) –N_2 adsorption
§ Not available (n/a)

surface areas three times higher than those of surrounding Oxisols, and had field capacity moisture content increased by 18 %. Tryon (1948) studied the effect of charcoal on the percentage of available moisture in soils of different textures and found different response among soils. In sandy soil, the addition of charcoal increased available moisture by 18 % (after adding 45 % biochar by volume), while no changes were observed in loamy soil, and soil available moisture decreased in the clay soil. Therefore, improvements in soil water retention by biochar additions may only be expected in coarse-textured soils or soils with large amounts of macropores. Additionally, a large amount of biochar may need to be applied to the soil before it increases water retention.

2.4.2.3 Soil nutrient supply

Nutrient availability can be affected by increasing cation exchange capacity, altering soil pH, or direct nutrient contributions from biochar. Biochar may supply a source of plant-available nutrients once applied to the soil (Gaskin et al. 2008; Sohi et al., 2010). The nutrient content of the original feedstock resources determines the nutrient concentration of the biochar (Table 2.3). Biochar has the potential to increase nutrient availability for plants (Lehmann et al., 2003; Chan et al., 2007; Spokas et al., 2012) once applied. Nutrients may be retained in biochar in a potentially extractable form, but it is uncertain whether these soluble nutrients are released instantaneously once added to the soil environment, or if they are released over time (Sohi et al., 2010), or if at all.

The rapid introduction of readily available nutrients and small amounts of labile C retained in biochar could promote mineralization of SOM (Wardle et al., 2008), especially in nutrient-limited tropical environments. For instances, Brewer et al. (2012) amended a semi-arid sandy Mollisol with 10 t ha^{-1} biochar made under various pyrolysis conditions, and generally observed an increase in soil extractable P, K, Mn, and Fe compared with unamended soil. Sinclair et al. (2010) amended solid cattle manure biochar in a field study on a Ferrosol and reported an increase in plant available P but the same soil amended with greenwaste biochar did not show increase in plant available P. In contrast, high rates of biochar application (4.4 % and 11 %, w/w) to a Sandy Yellow Earth resulted in a small but statistically significant reduction in plant available P (Van Zwieten et al., 2010b). Yao et al. (2009) studied the artificial aging of

biochar in the presence of humic substances and found immobilization of N, and increased availability of other nutrients, particularly P, Ca, Mg, and K.

Lentz and Ippolito (2012) examined hardwood-derived biochar application (22.4 t ha^{-1}) to a temperate Aridisol, noting an increase in soil-extractable Mn over a 2-yr period. More important, biochar applied with manure (42 t ha^{-1}) reduced manure organic C losses. In this calcareous system, the authors did not observe a change in soil pH, cation, or P availability as is typically noted in more acidic, weathered soils. Ippolito et al. (2012c) added switchgrass biochar pyrolyzed at two different temperatures (250 and 500 °C) to two Aridisols at the rate of 40 t ha^{-1}. The authors noted a two to threefold decrease in leachate P concentrations with the lower versus higher temperature biochar. This was attributed to retention of orthophosphate by surface functional groups, Fe and Al (hydro) oxide sorption, and Ca and Mg phosphate precipitation (Novak et al., 2009a).

2.4.2.4 Cation exchange capacity and nutrient retention

Soil amended with biochar is shown to have higher nutrient retention than unamended soils. One probable mechanism reported in most literature is via the enhancement of CEC by adding biochar as compared to unamended soils (Tryon, 1948; Mbagwu and Piccolo, 1997; Lehmann et al., 2003; Liang et al., 2006; Joseph et al., 2010; Laird et al., 2010). Biochar can adsorb and retain cations in an exchangeable form due to its great surface area and negative surface charge (Liang et al. 2006). Several reports have shown a significant increase in the availability of all major cations (Glaser et al. 2002; Lehmann et al., 2003) after biochar addition. Cation exchange capacity of biochar is highly variable depending upon the pyrolysis conditions under which it is produced. Freshly produced biochars have little ability to retain cations resulting in minimal CEC (Cheng et al., 2006; Lehmann, 2007a; Cheng et al., 2008), but are believed to increase with time in soil with surface oxidation (Cheng et al., 2006). This supports the findings of high CEC observed in Amazonian Anthrosols (Liang et al., 2006). In addition, Cheng et al. (2008) reported freshly produced biochar to exhibit an anion exchange capacity at pH 3.5, which decreased to zero over time as it aged in soil.

2.4.2.5 Sorption affinity, nutrient retention and reduced leaching

Compared to other forms of soil amendments, biochar is reported to have a higher sorption affinity for a range of organic and inorganic compounds, and higher nutrient retention ability (Bucheli and Gustafsson, 2000; Bucheli and Gustafsson, 2003; Allen-King et al., 2002; Nguyen et al., 2004). Abiotic and biotic surface oxidation of biochar results in increased surface carboxyl groups, a greater negative charge, and subsequently an increasing ability to sorb cations (Cheng et al., 2006; Cheng et al., 2008;). It also exhibits an ability to sorb polar compounds including many environmental contaminants (Yu et al., 2006).

It has been noted that biochar at high application rates (10 % or 20 %, w/w) can effectively increase sorption capacities and reduce NH_4^+ leaching (Lehmann et al., 2003) depending on biochar type and soil and their aging. Singh et al. (2010a) amended an Alfisol with wood and poultry litter based biochars produced at 550 °C and observed that freshly added biochars had little effect on NH_4^+ leaching, but upon aging in soil (around 5 months), reduce leaching of NH_4^+ by 55-65 %. In contrast, however, no sorption effects have been observed with biochars produced from the same feedstocks at 400 °C. They also tested all four biochars (two feedstocks and two temperatures) on a Vertisol, a soil inherently less prone to NH_4^+ leaching due to high smectite content in the clay fraction (Singh and Heffernan, 2002), and reported that all four biochars significantly reduced NH_4^+ leaching. Ding et al. (2010) investigated the adsorption properties of bamboo charcoal and its influence on N retention using multilayered soil columns in a Chinese Ultisol. They observed that biochar adsorbed NH_4^+ predominantly by cation exchange. Ammonium concentrations showed significant differences at different depths after NH_4Cl application depending on whether biochar had been added. In addition, application of biochar reduced overall cumulative losses of NH_4^+ via leaching at 20 cm depth by 15%. They suggested that biochar could be used as a potential nutrient-retaining additive, in order to increase the utilization efficiency of chemical fertilizers used for tropical Ultisols.

Sarkhot et al. (2012) applied dairy manure effluent enriched biochar at 20 t ha^{-1} on an arid California Alfisol. In this study, N leaching losses of biochars were similar to unamended soil, suggesting that biochar either acts as a slow release source of N or that it caused N immobilization. Schomberg et al. (2012) added nine different biochars to a South Carolina Ultisol at a rate equal to ~40 t ha^{-1}, incubating and leaching the soils over a 127 d period. They

found some biochars reduced N leaching losses, but soil N fractions were not increased with biochar application. Much of the apparent reductions in leaching were attributed to NH_3 volatilization loss arising from amendment with high ash biochars. Biochar ash content and pH are dependent on feedstock and pyrolysis temperature (Gaskin et al., 2008; Novak et al., 2009b).

2.4.2.6 Biochar liming type effect

The carbonate concentration of biochar is likely to keep a neutral or acidic soil pH to a more alkaline pH. This increased pH can subsequently stimulate microbial activity, thereby further promoting mineralization of existing SOM and increasing nutrient availability (Glaser et al. 2002; Lehmann and Rondon, 2006; Van Zweiten et al., 2007). The carbonates in biochar are easily released into the soil over time (Yuan et al., 2011b) and the ameliorating effects of biochar on soil pH is proportional to the application rate (Yuan et al., 2011a, Yuan et al., 2011c, Hass et al., 2012), especially in highly weathered tropical soils (Glaser et al., 2002). Mbagwu and Piccolo (1997) reported an increase of pH in various soils by up to 1.2 pH units from pH 5.4 to 6.6. Several reports have confirmed the liming type effect of biochar on acidic Ultisols (Yuan and Xu, 2011; Yuan et al. 2011b). The improvement of crop growth from biochar amendment in a typical Ultisol may result from an increase of pH and CEC (Peng et al., 2011). The liming of acidic soils decreases Al saturation, while increasing CEC and base saturation. (Mbagwu and Piccolo, 1997; Fisher and Binkely, 2000). In an 8 week incubation study, Hass et al. (2012) evaluated slow-pyrolysis chicken manure biochars (produced at 350 and 700 °C), amended at 5, 10, 20, and 40 g kg^{-1} with or without agronomic dolomitic lime (AgLime) into a highly weathered acid Gilpin soil (fine-loamy, mixed, active, mesic Typic Hapludult). Soil amended with a high rate of biochar (40 g kg^{-1}) produced from higher temperatures (700 °C) increased soil pH from 4.8 to 6.6 at the high application rate but was less effective than AgLime. They concluded biochar effect on soil pH was process-and rate-dependent. However, the liming type effect associated with biochar may not be ideal for all soil types and plant communities. Increased soil pH associated with biochar additions has caused micronutrient deficiencies in agricultural crops (Kishimoto and Sugiura, 1985).

2.5 Biochar effects on crop yield

Biochars have been reported to improve soil quality conditions and crop growth when used as a soil amendment alone or in combination with organic and inorganic fertilizers (Iswaran et al., 1980; Glaser et al., 2002; Lehmann et al., 2003; Chan et al., 2007; Chan et al., 2008; Graber et al., 2010; Ippolito et al., 2012). Many investigations have been conducted to study plant growth responses in both temperate and tropical soils. Hence, the specific mechanisms underlying the contribution of biochar to plant responses in different climatic regions are poorly understood. It appears from the literature that most of the plant responses are positive in the tropics and subtropics but mixed responses are reported in the temperate and arid climates (Tables 2.4 and 2.5). Variable responses may be explained in part due to different biomass feedstocks and the reaction conditions producing biochars with different physical and chemical properties (Keiluweit et al., 2010; Spokas et al., 2012), giving them varying effects in the soil (Chan et al., 2007; Chan et al., 2008; Rajkovich et al., 2012). This has been covered in detail in previous section of this chapter. It is also apparent from the literature that biochars may have direct effects on plant growth due to their inherent nutrient content, as well as many indirect effects, including improved retention of nutrients, and moisture (Lehmann et al., 2003; Lehman, 2007a; Lehman, 2007b; Spokas et al., 2012); enhancements in soil pH (Rondon et al., 2007); increased EC of leachate attributed to loss of Na and K from the biochar-soil matrix (Lehmann et al., 2003; Novak et al., 2009a); augmented soil CEC (Liang et al., 2006); improved soil physical properties (Lehman, 2007a, Chan et al., 2008); alteration of soil microbial populations and functions (Pietikainen et al., 2000; Graber et al., 2010; Lehmann et al., 2011); and increased crop protection from soil born diseases (Elad et al., 2010). In addition, regional climatic conditions including soil type, chemistry, temperature, and humidity also affect biochar agronomic benefits.

2.5.1 Plant growth responses following biochar additions to soils

The primary objective of soil amendment with biochar is to improve soil quality and crop productivity in a range of soils (Kimetu et al., 2008; Blackwell et al., 2009). This has been established primarily in tropical soils that are highly weathered or degraded (Kimetu et al., 2008). Much of the early information regarding biochar effects on soil parameters and agronomic yield and response has come from studying properties of Amazon Dark Earth Anthrosols and comparison to surrounding Oxisols (Laird et al., 2009). The Anthrosols of Amazonia region are

characterized by having enhanced levels of soil OM, higher CEC, pH, base saturation and nutrients such as N, P, K and Ca as compared to the surrounding Oxisols (Sombroek, 1966; Smith, 1980; Sombroek et al., 1993; Glaser et al., 2001; Lehmann et al., 2003; Liang et al., 2006). Furthermore, the higher crop yield on the Anthrosols relative to the adjacent Oxisols is attributed to the improved nutrient retention, and enhanced soil fertility of the Anthrosols over Oxisols (Lehmann et al., 2003; Liang et al., 2006; Solomon et al., 2007). It was found that these Anthrosols have C contents of up to 150 g C kg^{-1} in comparison to the surrounding Oxisols that have 20-30 g C kg^{-1} (Sombroek, 1966; Lehmann et al., 2003).

The response to biochar is dependent on mechanisms in the soil is influenced by biochar application (Glaser et al., 2001; Lehmann et al., 2003b). Despite the recalcitrant nature of biochar, it has the potential for abiotic and microbial oxidation and the formation of functional groups with net negative charge on biochar particle surfaces (Schmidt et al., 2002; Trompowsky et al., 2005) that can adsorb cations on their surfaces. Variation in pH influences the dissociation of proton-binding groups such as carboxyl groups on organic matter and surface OH^- groups on oxides and hydroxides. Besides the activities of OH^- and H^+ in the equilibrium solution, several anions can form ligands with oxide and hydroxide surfaces (potential determining ions) and thereby affect the cation and anion exchange capacity of soils (Hingston et al., 1971). The CEC is a chemically significant property, reflecting the buffering capacity of soil. Exchange reactions control the equilibrium between solid and liquid phases in soils, reducing fluctuations in ion concentrations.

Another important factor which is often neglected by most biochar literature is how soil mineralogy influences the CEC. Young volcanic soils are characterized by high organic content and an abundance of non-crystalline minerals (e.g., allophane, imogolite and ferrihydrite), which are the primary weathering products. These soils contain relatively amorphous minerals having a high degree of hydration, extensive surface area, and variable charge (Jackman, 1964; Wada, 1986). As a result, they can form stable organic–mineral bonds through anion and inner-sphere ligand-exchange reactions, and their geometry may be well suited for physically protecting SOC (Martin and Haider, 1986; Oades, 1994). Smectite, montmorillonite type minerals are metastable. Given enough time, they dehydrate to crystalline clays, including halloysite, kaolinite, gibbsite, goethite and haematite (Wada, 1986; Schwertmann and Taylor, 1989) that have a lower surface area and charge density, and consequently a lower affinity for SOM. Andisols contain twice as

much SOC per m^2 as do Oxisols or any other soil order except Histosols (Post, 1983). Tan and Dowling (1984) added fresh organic C to soils and found organic C can alter the charge distribution, and therefore the CEC value. Therefore, it is evident that soil mineralogy controls the charge and surface properties of soils in both temperate and tropical soils and the nature of control mechanisms is different for both climatic regions. When biochar is added to a soil rich in noncrystalline clay minerals, the soil might be able to stabilize a greater amount of C than crystalline mineral rich soils (Torn et al., 1997). However, there is not enough information found in the literature regarding the interaction between soil mineralogy and biochar particles.

2.5.2 Crop responses to biochar amendment of tropical soils

Many studies have been conducted with biochar to investigate the agronomic yield response and underlying response mechanism throughout the world. However, the majority of the reported studies have taken place in tropical environments (Table 2.4). Lima et al. (2002) studied BC rich tropical Anthrosols with high leaching conditions in humid tropical Amazonia in which they observed BC rich Anthrosols maintained high cation availability compared with adjacent forest soils with similar mineralogy. The finding of Lima et al. (2002) suggest that due to the prevalence of highly weathered clay minerals such as kaolinite in these soils, their ability to retain cations might be dependent entirely on SOM content (Sombroek, 1966; Sombroek et al., 1993). Such greater CEC could be created either by a higher degree of oxidation of aromatic C in SOC and formation of carboxyl groups (Glaser et al., 2003) or by an elevated surface area for cation adsorption sites, or a combined effect of both. This formation of carboxyl groups with net negative charge can be the product of surface oxidation of BC particles; or adsorption of highly oxidized organic matter onto BC surfaces (Lehmann et al., 2005). This is further confirmed by Liang et al. (2006) in their work with BC rich Anthrosols and adjacent soils of the Amazonia region of Brazil. This surface oxidation led to a higher CEC per unit C as well as to a higher charge density in BC-rich Anthrosols compared to BC-poor adjacent soils. Additionally, the Anthrosols showed a higher surface area due to their higher BC concentrations. Therefore, BC was more efficient in providing CEC and cation retention than non-BC in the studied tropical

Table 2.4. Biochar impacts on crop yields in the tropical regions of the world

Biochar feedstock	Pyrolysis (Temp. °C)	Application		Study type	Soil type	Crop	Biomass yield†		Country	References
		Biochar (t ha^{-1})	Fertilizer (kg ha^{-1})				Grain	Total		
Agricultural biomass sources										
Greenwaste biochar	n/a‡	10	100N	Pot trial in glass house	Alfisol	Radish	n/a	95 %	Australia	Chan et al., 2007
Rice husk	Gasification (900-1100)	50	Sediment (25)+ Compost (50)	Pot trial	Sandy loam	Lettuce	n/a	259 %	Cambodia	Carter et al., 2013
Rice husk	Gasification (900-1100)	50	sediment (25)+ Compost (50)	Pot trial	Sandy loam	Cabbage	n/a	111 %	Cambodia	Carter et al., 2013
Macadamia Nut shell	Flush carbonization (300-800)	(5% $^{w}/_{w}$)	400N+1500 P+200K	Pot trials in green house	Ultisol	Corn	n/a	-50 %	Oahu Island, USA	Deenik et al., 2010
Maize cob	Traditional Kiln (400)	0.8 and 4	154N+56P+ 28K+16.8S	Field trial	Ferrallic Arenosols; Haplic Luvisols	Maize	131-444 %	n/a	Zambia	Cornelissen et al., 2013
Rice Husk	Japanese traditional Kiln	41	60N+8.2P+ 25K	Field trial	Anthraquic Gleysols	Rice	-5 %	n/a	Philipines	Haefele et al., 2011
Rice Husk	Japanese traditional Kiln	41	40N+12P+10K	Field trial	Gleyic Acrisols	Rice	24 %	n/a	Thailand	Haefele et al., 2011

† % biomass yield as compared with control

‡ Not available (n/a)

Table 2.4. Continued

Biochar feedstock	**Pyrolysis** (Temp. °C)	**Application**		**Study type**	**Soil type**	**Crop**	**Biomass yield**†		**Country**	**References**
		Biochar (t ha^{-1})	Fertilizer (kg ha^{-1})				Grain	Total		
Agricultural biomass sources										
Wheat straw	350-550	10 and 40	300N+125P_2O_5+125K_2O	Field trial	Hydroagric Stagnic Anthrosola and Halpudept	Rice	9-12 %	n/a‡	China	Zhang et al., 2010
Wood (Forestry) sources										
Mixed softwood	Traditional Kiln (400)	0.8 and 4	154N+56P+28K+16.8S	Field trial	Ferrallic Arenosols; Haplic Luvisols	Maize	134-352 %	n/a	Zambia	Cornelissen et al., 2013
Teak	n/a	0, 4, and 8	50N	Field trial	Laotian paddy soil	Rice	n/a	-36-15 %	Laos	Asai et al., 2009
Eucalyptus	Kiln Pyrolysis (350°C)	120	300lime+20P+20 N	Green house pot trial	Clay–loam oxisol (Typic Haplustox)	Beans	n/a	39 %	Columbia	Rondon et al., 2007
Douglas-fir and ponderosa pine	350	2% ($^w/_w$)	none	Pot trial in green house	Sandy-skeletal (Typic Dystrustepts)	Perenial grass	n/a	24 %	USA	Gundale and DeLuca, 2007

† % biomass yield as compared with control
‡ Not available (n/a)

Table 2.4. Continued

Biochar feedstock	**Pyrolysis** (Temp. °C)	**Application**		**Study type**	**Soil type**	**Crop**	**Biomass yield**†		**Country**	**References**
		Biochar (t ha^{-1})	Fertilizer (kg ha^{-1})				Grain	Total		
Wood (Forestry) sources										
Eucalyptus	Traditional Kilin (400-500)	6	120N+100P+100K	Field trial	Ultisol	Corn	Non-significant	n/a‡	Kenya	Kimetu et al., 2008
Eucalyptus	n/a	16 and 32	100N+25P+15K	Field trial	Sandy loam soil	Upland rice	Significant (2nd year)	significant (2nd year)	Brazil	Petter et al., 2012
Eucalyptus	550	10 and 30	200N+80P+100K	Glasshouse pot trials	Sandy soil	Hybrid maize	n/a	Non-significant	Australia	Namgay et al., 2010
Oil mallee biochar from Eucalyptus	Open pan pyrolysis	6	8N+17.6P+7S+8.6Ca	Field trial	Sandy clay loam	Wheat	-3.60 %	n/a	Australia	Solaiman et al., 2010
Animal sources										
Poultry litter (Manure+Shaw dust)	Slow (500)	30	14N+50 P_2O_5-50 K_2O	Greenhouse polybag trial	n/a	Maize	n/a	1 %	Indonesia	Widowati et al., 2012
Poultry litter	450	10, 25, and 50	100N	Pot trial in glass house	Alfisol	Radish	n/a	42-96 %	Australia	Chan et al., 2008

† % biomass yield as compared with control

‡ Not available (n/a)

soils. In a pot experiment, Lehmann et al. (2003) found biochar to increase rice biomass by 17 % and cowpea by 43 % when applied at rates of 68 t C ha^{-1} to 135 t C ha^{-1}. This growth was attributed to direct nutrient additions from biochar of P, K and Cu. Other studies have attributed positive plant growth to positive changes in soil biogeochemistry as a result of biochar additions (Iswaran et al. 1980; Wardle et al. 1998; Hoshi 2001; Lehmann et al. 2003b; Chan et al. 2007; Van Zwieten et al., 2007). Iswaran et al. (1980) reported a 51 % increase in biomass in soybean crops with biochar additions of 0.5 t ha^{-1} and Hoshi (2001) found a 20 % increase in volume and 40 % increase in height of tea trees with biochar additions. Chidumayo (1994) reported better seed germination (30 % enhancement), shoot heights (24 %) and biomass production (13 %) among seven native woody plants on soils under charcoal kilns compared to the undisturbed Zambian Alfisols and Ultisols.

2.5.3 Crop responses to biochar amendment of temperate and arid soils

A number of investigations have been done to evaluate agronomic responses to biochar amendment in temperate and arid climates (Table 2.5), but the understanding of yield response mechanisms to added biochar in temperate climates is still ambiguous. Biochar addition to soils is known to affect the soil specific surface area and increase the adsorption sites of the soil. Curtin and Smillie (1976) studied 51 temperate Irish soils, with varying SOC (range 0.1-8.9 %), clay (range 0.4-56 %) and pH (range 3.8-8.3), and concluded that CEC was correlated with SOC (R^2 = 50 %) and specific surface area (R^2 = 66 %). Martel et al. (1978) in a study of 11 clay soils (40-51 % clay, mean 3.1 % SOC) concluded that only 10-15 % total CEC was associated with SOC. In these soils, surface area was better related to CEC than clay content, albeit on these clay-rich soils CEC was dominated by the mineral fraction. High CEC is a characteristic of temperate soils, especially those high in clay and OM.

Biochar is suggested to cause N immobilization and could potentially cause N deficiency in plants when applied to soil alone due to its high C: N ratio (Sullivan and Miller, 2001; Chan and Xu, 2009; Lehmann and Joseph, 2009), leading to further uncertainty regarding its effect on plant growth. Additions of OM with available C: N ratios above 20 are known to cause microbial N immobilization (Fisher and Binkley, 2000). Because biochar has a high C: N ratio (up to 400), it is possible that decomposition of its labile C fraction could contribute to a reduction in soil

Table 2.5. Biochar impacts on crop yields in the temperate regions of the world

Biochar feedstock	Pyrolysis (Temp. °C)	Application		Study type	Soil type	Crop	Biomass yield†		Country	References
		Biochar (t ha^{-1})	Fertilizer (kg ha^{-1})				Grain	Total		
Agricultural biomass sources										
Wheat straw	370	0, 0.5, 1, 2.5 % ($^{w}/_{w}$)	0N+58P+144K per pot	Growth chamber pot trial	Loamy sand	Durum wheat	-3-41 %	No significant response	Spain	Alburquerque et al., 2013
Peanut hull	Steam (400)	11.4	26N+122 P_2O_5+167 K_2O	Field trial	Loamy sand	Corn	-35 %	5 %	USA	Gaskin et al., 2010
Sugarcane bagasse	Fast (600)	3 % ($^{w}/_{w}$)	240 N	Field trial	Heavy clay	Sugarcane		6 %	Japan	Chan et al., 2010
Corn stover	Slow (300, 400 & 500)	2.6, 6.5, 26, 91	12N+10P+10K	Greenhouse pot trials	Silt loam and loam	Corn	n/a‡	30 %	USA	Rajkovich et al., 2012
Wood (Forestry) sources										
Willow	n/a	5 % ($^{w}/_{w}$)	none	Greenhouse pot trial	Calcarious Brown loam	Maize	n/a	28 %	Ireland	Kwapinski et al., 2010
Pine	n/a	5 % ($^{w}/_{w}$)	none	Greenhouse pot trial	Calcarious Brown loam	Maize	n/a	35 %	Ireland	Kwapinski et al., 2010
Miscanthus	n/a	5 % ($^{w}/_{w}$)	none	Greenhouse pot trial	Calcarious Brown loam	Maize	n/a	53 %	Ireland	Kwapinski et al., 2010

† % biomass yield as compared with control

‡ Not available (n/a)

Table 2.5. Continued

Biochar feedstock	Pyrolysis (Temp. °C)	Application		Study type	Soil type	Crop	Biomass yield†		Country	Reference
		Biochar ($t\ ha^{-1}$)	Fertilizer ($kg\ ha^{-1}$)				Grain	Total		
Wood (Forestry) sources										
Coppice woodland (Beech, Hazel, Oak, Birch	Fast (500)	30	122N+50 P_2O_5	Field trial	Silty loam	Durum wheat	28%	28%	Italy	Vaccari et al., 2011
Japanese oak (Leaves)	Traditional klin	10% ($^{v}/_{v}$)	10N+10P +10K	Greenhouse pot trial	Potting mix	French marigold	n/a‡	No significant response	Japan	Kadota and Niimi, 2004
Olive stree prunning	450	0, 0.5, 1, and 2.5% ($^{w}/_{w}$)	0N+58P+ 144K per pot	Growth chamber pot trial	Loamy sand	Durum wheat	-3-41%	No significant response	Spain	Alburquerque et al., 2013
Pine chip	Steam (400)	11.4	26N+122 P_2O_5 + 167K_2O	Field trial	Loamy sand	Corn	-23%	-6%	USA	Gaskin et al., 2010

† % biomass yield as compared with control
‡ Not available (n/a)

Table 2.5. Continued

Biochar feedstock	Pyrolysis (Temp. °C)	Application		Study type	Soil type	Crop	Biomass yield†		Country	References
		Biochar (t ha^{-1})	Fertilizer (kg ha^{-1})				Grain	Total		
Animal sources										
Chicken manure	450	22.8	83K	Green house pot trial	Sandy loam	Soy-bean	9 %	40 %	Japan	Tagoe et al., 2008
Poultry litter	Slow (300, 400 and 500)	2.6, 6.5, 26, and 91	12N+10 P+10K	Green house pot trial	Silt loam and Loam	Corn	n/a‡	17 %	USA	Rajkovich et al., 2012
Cattle manure	Slow (300, 400 and 500)	2.6, 6.5, 26, and 91	12N+10 P+10K	Green house pot trial	Silt loam and loam	Corn	n/a	43 %	USA	Rajkovich et al., 2012
Cow manure	500	10	none	Green house pot trial	Dryland sandy soil	Maize	7 %	n/a	Japan	Uzoma et al., 2011

† % biomass yield as compared with control
‡ Not available (n/a)

mineral N. However, the total C and N content in biochar does not reflect the actual availability of the C and N for microbes to cause immobilization. Gajić and Koch (2012) worked with German Luvisol amended with 10 t ha^{-1} of either sugar beet (*Beta vulgaris* L.) pulp or beer draft hydrochar and grew sugar beet. They suggested that hydrochar can decrease plant available N due to N immobilization. Lentz and Ippolito (2012) made a onetime application of hardwood biochar at 22.4 t ha^{-1} to an Aridisol, and found no change in corn (*Zea mays* L.) silage yield as compared to a control in the first year following biochar application; however, they did observe a 36 % yield decrease in the second year and concluded that the suppression in yield was due either to reduced nutrient (e.g., N, S, Mn, and Cu) availability or nutrient uptake by the corn. The response observed by Lentz and Ippolito (2012) was similar to a priming effect observed in low organic C-containing soils (Zimmerman et al., 2011) where the biochar may have induced a reduction in soil C mineralization, which in turn limited soil N and S availability.

Schnell et al. (2012) applied up to 3 t ha^{-1} of sorghum [*Sorghum bicolor* (L.) Moench] biochar to an Alfisol and then grew sorghum for 45 d and found no significant difference in biomass production between treatments and concluded that low nutrient uptake and recovery in plants grown in biochar-treated soil could have contributed to a lack of yield response. In contrast, Kammann et al. (2012) added peanut (*Arachis hypogaea* L.) hull biochar at 50 t ha^{-1} to a German Luvisol followed by ryegrass (*Lolium perenne* L.) and observed a significant increase in biomass yield when compared to controls. The cause of the increase in yield was attributed to reduced N loss to denitrification and hence greater N uptake by plants grown in the presence of biochar.

2.6 Conclusion

The quality of biochar for amendment of agricultural soils largely depends on type of biomass feedstocks and production conditions. Plant biomass has a complex composition, mainly comprised of hemicellulose, cellulose, and lignin. Cellulose and lignin were found to impact the yield and quality of the produced biochar. For biochar production, slow pyrolysis is currently viewed as the preferred technology as it maximizes biochar yield and reactive surface functional groups. Understanding interactions among biomass feedstock, biochar production and application conditions, soil texture, OM, and soil pH will be a key factor in determining long-term effects of biochar application on agricultural crops. Biochar was found to be effective in

increasing pH of acidic soils due to the liming type capacity and enhanced CEC. Aging in soil can further increase CEC and sorption ability. This can improve the availability of some nutrients, which is commonly thought to be responsible for positive plant growth responses to biochar amendments. Reduced leaching loss of nutrients (e.g. NH_4^+) is commonly reported in biochar amended soils. However, it can be difficult to differentiate among direct and indirect factors and mechanisms affected by biochar amendment that influence agronomic response. Almost no information is currently available on how biochar characteristics affect microbial-mediated nutrient cycling and soil microbial communities. It seems apparent that positive crop yield responses are most consistently observed in tropical environments with highly weathered acidic soils. Future research should focus on a better understanding of biochar-plant interactions in different climatic regions to develop recommendations for application, especially to increased yield in temperate soils. Further research needs to fully elucidate relationships between biochar characteristics, climatic conditions, soil properties and their influence on nutrient leaching, retention, and immobilization.

3. Effects of Biochar on Yield, Nutrient Recovery, and Soil Properties in a Canola-Wheat Rotation Grown under Controlled Environmental Conditions

3.1 Preface

It is well established that amending soil with biochar can potentially have beneficial impacts on plant growth and soil properties. Investigating the effects of biochar on crop growth has mainly concentrated on nutrient poor soils in sub-tropical and tropical regions, and little is known about its effect on the northern Great Plains soils. Understanding the characteristics of different biochars and evaluation of their effects on soils and crop yield in prairie soils is needed to better assess the utility of biochar as a soil amendment. The research described in this chapter is a first attempt to address the response of canola (*Brassica napus* Invigor 5030) and wheat (*Triticum aestivum* Prodigy) grown in rotation to different biochar sources and rates alone and in combination with commercial fertilizer in a growth chamber. Evaluation under controlled conditions provides valuable data to compare with the field studies conducted with similar treatments (Chapter 4) but under variable environmental conditions.

3.2 Abstract

Biochar derived from pyrolysis of biomass feedstocks have proven effective in highly weathered tropical soils. However, less is known about how biochars behave as amendments when added to temperate soils. Previously, studies have used high rates (tens to hundred t ha^{-1}) but such high rates are impractical when the biochar is in a powdery form. Moreover, there is inadequate knowledge of the impacts of different biochars produced from different feedstocks. Therefore, a study was conducted to evaluate the response of canola and wheat to two different rates of five different biochars added to a Brown and Black Chernozem soil in a controlled environment experiment. Biochars were obtained from three different feedstock sources: 1) wheat straw used to produce fine fraction fast pyrolysis and chunky fraction slow pyrolysis char; 2) flax straw to produce fine fraction fast pyrolysis char, and 3) willow fine fraction slow pyrolysis and chunky fraction slow pyrolysis biochars. Biochar was added at 1 and 2 t ha^{-1}

without and with nitrogen (N) and phosphorus (P) fertilizer at a rate of 50 or 100 kg N ha^{-1} and 25 kg P_2O_5 ha^{-1}. Canolas followed by wheat were each grown in an amended pot over a four week period. Biochar application was found to have variable effects on canola biomass yield while wheat grown in rotation did not show any response except FSB-fine biochar. Biochar application resulted in significant increases in canola biomass yield for the two fast pyrolysis biochar types added to CLC-Black soils, while the other three biochar types had no effect on yield. For the following wheat crop, only FSB-Fine biochar added at 1 t ha^{-1} had a significant residual effect on biomass yield. Occasional depressions in crop biomass yield were observed. In these calcareous Chernozems, biochar did not greatly alter the availability of N and P, and its effects on soil pH, organic carbon, and electrical conductivity, were small and often non-significant. We suggest that biochar applications at rates of 1-2 t ha^{-1} to prairie Chernozems will not have large effects on soil properties or plant growth when grown under in the growth chamber.

3.3 Introduction

Biochar is a carbonaceous solid material produced by heating biomass in an oxygen (O_2) limited environment through a pyrolysis process. It is intended to be added to soils as a means to sequester carbon (C) and maintain or improve soil functions. A detailed review of biochar manufacture, properties, and effects on soil and plant growth is provided in Chapter 2. The physical and chemical properties of biochar impact the way biochar functions within the soil system. The key physical features of biochar are the low biodegradability, high porosity, and high surface area which can affect nutrient retention. Biochar incorporation can alter soil physical properties such as structure, pore size distribution and density, with implications for soil aeration, water holding capacity, plant growth, and soil workability (Downie et al., 2009). Evidence suggests that biochar application to soil may alter bulk density, increase net soil surface area (Chan et al., 2007) and consequently, may improve soil water and nutrient retention (Downie et al., 2009; Ding et al., 2010). Biochar may supply a source of plant-available nutrients once applied to the soil (Gaskin et al., 2008; Sohi et al., 2010), although no direct nutrient contribution was reported for a biochar derived from oat hulls that was added to a Saskatchewan soil (Stefankiw, 2012). Soil amended with biochar was shown to have higher nutrient retention than unamended soils. One probable mechanism reported in the literature is to enhance nutrient

sorption and alter pH (Tryon, 1948; Mbagwu and Piccolo, 1997; Lehmann et al., 2003; Lehmann and Rondon, 2006; Liang et al., 2006; Van Zweiten et al., 2007; Joseph et al., 2010; Laird et al., 2010; Van Zweiten et al., 2010a).

Investigations of the effects of biochar amendments on crop growth have increased in number over the past years and have mainly concentrated on tropical soils (Lehmann et al., 2003; Yamato et al., 2006; Chan et al., 2007; Steiner et al., 2007; Chan et al., 2008; Kimetu et al., 2008; Gaskin et al., 2010; Major et al., 2010; Van Zwieten et al., 2010a; Van Zwieten et al., 2010b). Much of the early information regarding biochar effects on soil parameters and agronomic yield response has come from studying properties of Amazon Dark Earth Anthrosols and surrounding Oxisols (Laird et al., 2009). An important aspect for improving crop growth in highly weathered soils is the liming type effect of biochars (Yamato et al., 2006; Van Zwieten et al., 2010a; Yuan and Xu, 2011) and the generation of cation exchange capacity (CEC) to reduce nutrient leaching (Lehmann et al., 2003; Liang et al., 2006). Pot trials conducted on a nutrient depleted Alfisol showed that there were no significant increases in plant yield with the application of biochar alone, however biochar plus nitrogen (N) fertilizer trials produced a significant increase in plant yield (Chan et al., 2007). In addition to the reported beneficial effects on soil productivity, some biochars have shown negative effects, with reduced plant growth and yield (Devonald, 1982; Gaskin et al., 2010; Gajić and Koch, 2012; Lentz and Ippolito, 2012; Schnell et al., 2012; Kloss et al., 2013).

In general, there is a lack of studies that investigate biochar effects on crop growth in temperate soils that are not primarily limited by pH or CEC. As well, most of the studies have been conducted with very high rates of biochar application, but such rates may be considered impractical for application of dry chars due to the very low density and powdery nature that makes them difficult to transport and apply, especially in the windy southern Canadian prairies. An evaluation of the effects of biochars on crops and soils of the Canadian prairies is needed to predict potential benefits of biochar as a soil amendment in this region of the world. The general objective of the study was to evaluate the effectiveness of different biochars as soil amendments to improve soil conditions for crop growth, with emphasis on soil fertility impacts. Two soils were chosen for the study to provide a contrast in soil properties, and provide representation of the southern and northern agricultural regions of Saskatchewan. The specific objectives of the study were to investigate the effects of amendment with five different biochars applied at two

rates on canola (*Brassica napus* Invigor 5030) and wheat (*Triticum aestivum* Prodigy) biomass yield, uptake and recovery of N and phosphorus (P) in two contrasting Saskatchewan soils under controlled environment conditions in a growth chamber; and to evaluate the effect of biochars on soil properties, including available nutrients, soil organic carbon (% OC), pH and electrical conductivity (EC) at the end of the growth period.

3.4 Materials and methods

3.4.1 Study site and biochar production

Orthic Brown and Black Chernozems agricultural soil were collected in spring 2011 from two different locations in the agricultural region of Saskatchewan, Canada (Fig. 3.1). Approximately 200 kg of soil were removed from the 0-15 cm depth in the field with a hand shovel. The soil was placed in plastic rubbermaid containers and returned to the laboratory in Saskatoon where it was air-dried and then homogenized in a soil mixer. The Brown Chernozem site is located on a farm about 5 km southeast of Central Butte, Saskatchewan, Canada (legal location SW31-20-3-3) in the southern mixed grass prairie region. The soils in this area are dominated by Brown Chernozems (Aridic Borolls). The field research site is classified as a mixture of Kettlehut and Ardill soil associations. The Kettlehut soil association is predominantly a Brown Solod to a Brown Solodized Solonetz, and the Ardill soil association is dominantly an Orthic Brown to a Calcareous Brown Chernozem (Soil Classification Working Group 1998). The actual location where the soil was sampled from is of Ardill association. The parent material is moderately-fine-textured, moderately-calcareous glacial till with a loam soil texture.

The Black Chernozem site is located at the Conservation Learning Center (CLC) research farm, about 18 km south of Prince Albert (legal location SE20-46-26-W2), in the parkland region of Saskatchewan, Canada. It features rolling topography, wetlands and remnant native upland areas. The soil that was sampled at the site is classified as an Orthic Black Chernozem, Meota association (Typic Cryoboroll) of sandy loam texture, on a gently sloping topography. Both the soil and landscape are typical of the region in the northern agricultural region of Saskatchewan. Lehmann (2007a) stated that the addition of C as biochar is likely to have more benefit in a soil with low organic matter (OM) content than high OM content. Therefore, the Brown Chernozem (CB-Brown) with low OM content (2 %) and the Black Chernozem (CLC-Black) with relatively

higher OM content (5 %) provide a good contrast in soil organic carbon (SOC) contents for the study.

Fig. 3.1. Locations of two study sites in Saskatchewan, Canada. ArcGIS10 (Environmental Systems Research Institute, Inc., Redlands, CA, USA) map courtesy of Dr. Beyhan Amichev.

A total of five biochars were obtained from three different feedstock sources: wheat straw (*Triticum aestivum* L.), flax straw (*Linum usitatissimum* L.), and willow stems (*Salix spp.)* The three different feedstocks were used to produce five different biochars. Among the five biochars tested, the Saskatchewan Research Council (Saskatoon, SK, Canada) provided fast pyrolysis wheat straw fine fraction biochar (WSB-Fine) and fast pyrolysis flax straw fine fraction biochar (FSB-Fine). They also supplied slow pyrolysis willow fine fraction biochar (WB-Fine), and slow pyrolysis willow chunky fraction biochar (WB-Chunky). Prairie Biochar Inc. (Regina, SK, Canada) supplied a slow pyrolysis wheat straw chunky fraction (WSB-Chunky). During the fast pyrolysis process, the reactor temperature was ~ 400 °C with residence time less than 1 min, whereas for the slow pyrolysis reactor temperature varied between 300 °C to 600 °C with residence time less than 60 min.

3.4.2 Soil and biochar characterization

The basic soil characteristics of CB-Brown and CLC-Black soils used in this study are summarized in Table 3.1. Both soils are loamy in texture and relatively low in available N with moderate contents of extractable available P and sulfur (S). The CB-Brown soil is especially low in SOC. The pH of CB-Brown soil is neutral to slightly basic and the CLC-Black soil is slightly acidic to neutral. Electrical Conductivity is low (rated as non-saline) in both Brown and Black soils. Both soils have a higher content of exchangeable calcium (Ca) than other cations.

Table 3.1. Soil properties of soils used in the growth chamber studies

Soil	Texture	NO_3†	PO_4†	SO_4†	Exchangeable Cations‡				OC	pH§	EC¶
					Ca	Mg	Na	K			
		----------	----------	----------	mg kg^{-1}	----------	----------	----------	(%)		(ds m^{-1})
CB-Brown	Loam	7.8	17.4	7	2569	550	1130	730	1.6	8.0	0.1
CLC-Black	Loam	6.2	11.2	7	3755	648	290	438	4.3	6.5	0.1

† Extractable NO_3^--N, PO_4^+-P and SO_4^+-S
‡ Extractable cations
§ pH of a 1:2 (soil:water) extract
¶ Electrical conductivity of a 1:2 (soil:water) extract

Air dried biochar samples were analyzed and their properties are summarized in Table 3.2. All biochars had pH>7 and are considered alkaline. The least alkaline was the fast pyrolysis FSB-Fine biochar (pH 8.6) while the most alkaline was the slow pyrolysis WB-Fine biochar (pH 10.3). The two fast pyrolysis biochars (WSB-Fine and FSB-Fast) had similar CEC values (36 and 32 cmol kg^{-1} while the slow pyrolysis WB-Fine was highest (54 cmol kg^{-1}). The slow pyrolysis WB-Chunky had the lowest CEC. Specific Surface Area (SSA) was determined with the N_2 adsorption method according to Brunauer et al. (1938). The fast pyrolysis biochars (WSB-Fine and FSB-Fast) had similar SSA's (1.03-3.02 m^2 g^{-1}) while the values for WB-Fine and WB-Chunky were approximately two orders of magnitude greater.

Table 3.2. Physical and chemical characteristics of different biochars

Parameters	**Biochar type**†				
	WSB-Fine	**FSB-Fine**	**WB-Fine**	**WB-Chunky**	**WSB-Chunky**
Pyrolysis	Fast	Fast	Slow	Slow	Slow
SSA‡ (m^2 g^{-1})	2.4	1.0	238.4	175.0	n/d§
pH (H_2O)	9.2	8.6	10.3	9.7	n/d
VM¶ (%)	24.1	29.7	15.5	12.8	n/d
TOC (%)	68	73	62	84	n/d
CEC (cmol kg^{-1})	36	32	54	11	n/d
Ash (%)	15	8	25	11	n/d
TN# (%)	0.9	1.4	1.1	0.7	0.8
P_2O_5†† (%)	2.4	6.2	2.7	4.0	n/d
TS‡‡ (%)	0.15	0.14	0.08	0.04	0.86

† WSB-Fine = Wheat straw fine fraction fast pyrolysis biochar; FSB-Fine = Flax straw fine fraction fast pyrolysis biochar; WB-Fine = Willow fine fraction slow pyrolysis biochar; WB-Chunky = Willow chunky fraction slow pyrolysis biochar; and WSB-Chunky = Wheat straw chunky fraction slow pyrolysis biochar

‡ Specific surface area; air-dried samples were analyzed by Pore Science Labs, Bristol, PA; and measured based on Brunauer–Emmett–Teller (BET) –N_2 adsorption. For others, by Loring Laboratories, Calgary, Alberta

§ Not determined (n/d)

¶ Volatile Organic Matter

Total Nitogen

†† In Ash

‡‡ Total Sulphur

3.4.3 Experimental design

The pot studies were carried out under controlled environment (growth chamber or phytotron) conditions. Biochars were added to the two soils (CB-Brown and CLC-Black) at three biochar application rates (0, 1, and 2 t ha^{-1}) alone and in combination with 50 (low rate) or 100 (standard or typical rate) kg N ha^{-1} as urea (46-0-0) and 25 (typical rate) kg P_2O_5 ha^{-1} as mono ammonium phosphate (12-51-0). The rates of biochar were selected to represent rates that could be practically applied in the field. With four replicates of each treatment, this provided a total of 72 pots for each soil type. Given the restricted availability of growth chamber space, the experiment was conducted with one biochar source at a time with 4 replications of each treatment.

Pots were prepared with 900 g of air-dried soil mixed thoroughly with the biochar and fertilizer treatments. Soils were ground and brought to 50 % of the field capacity before seeding. Ten canola seeds were broadcast over the surface of the pot and then another 100 g of soil was placed on the surface to make sure all the seeds were at a depth of at least 2 mm. Then sufficient water was added to bring the entire soil to 85 % of field capacity. Once the seedlings emerged, germination counts were done, and following germination, the plants were thinned to three canola plants per pot. Then, pots were transferred to the growth chamber.

The pots were arranged in a completely randomized design and were rotated each week during the four week growth period. Growth chamber conditions were maintained on a 16/8 h day-night length cycle. The day and night temperature of the growth chamber was 22 and 13 °C respectively. Relative humidity was maintained at 50 % and light intensity was maintained at 615.6 µmol m^{-2} s^{-1}. The plants were watered regularly with distilled water to maintain them at 85 % field capacity. After four weeks of growth, the above-ground biomass of the canola plants were harvested at soil level and the same pots were used for seeding wheat. During seeding, ten wheat seeds were pressed down into the soil at a depth of about 2 mm, and then sufficient water was added to bring them to 85 % field capacity. Once the seedlings emerged, germination counts were done and the wheat plants were thinned to five plants per pot. A similar procedure as described for canola was maintained for wheat throughout the four weeks of the wheat growth period. During the growth period, the pots were monitored for plant health weekly. The above-ground biomass was harvested upon completion of the growth period by cutting the entire plants

at soil level and the plant materials were oven-dried at 50 ^{o}C, weighed for dry matter yield, and ground using a Cyclone^{TM} grinder for nutrient analysis. The plant materials were analyzed for N and P concentration.

3.4.4 Soil and plant analyses

Soil samples from each treatment were collected after canola harvest by taking four small (1 cm) cores from the surface to the pot bottom at random locations. The four cores were then combined to provide a single composite sample from each pot that was air-dried and ground. After the final harvest of wheat, the entire amount of soil in the pot was removed, air-dried, ground, and sieved in preparation for laboratory analysis. Basic soil characteristics of the two soils used in the growth chamber were determined in a sub-sample of the soil collected from the field following drying and homogenization. Soil texture was determined by a laser scattering particle size distribution analyzer (HORIBA© LTD., 2007). Electrical conductivity and pH were measured by the glass electrode method using 1: 2 soil: water suspension (Nelson and Sommers, 1982). Soil organic carbon was measured using the Leco C632 carbon combustion analyzer (LECO© Corporation, 2007) following the protocols of Wang and Anderson (1998).

Total N and P in plant samples were determined by standard H_2SO_4-H_2O_2 digestion as described by Thomas et al. (1967). For these measurements, 0.25 g of plant sample was weighed into 75 mL digestion tubes, 5 mL of concentrated H_2SO_4 was added in each digestion tube, and this suspension was heated at 360 ℃ for 30 min and then allowed to cool. This was repeated five times. The N and P in the extracts were measured using a Technicon Autoanalyzer II segmented flow automated colorimetry system.

The Modified Kelowna (MK) extractions were conducted in all soil samples according to the procedure by Qian et al. (1994). The extractant was prepared by combining 28 mL of 0.25 *M* acetic acid, 38.5 g of 0.25 *M* ammonium acetate, and 1.11 g of 0.015 *M* ammonium fluoride into a 2 L volumetric flask. Soil samples (3 g) was weighed into 100 mL plastic containers, and 30 mL of the MK extracting solution was dispensed into each of the containers and then shaken horizontally in a rotary shaker at 160 RPM for 5 min. The extract was filtered using a VWR® # 454 filter paper into 7 Dram vials and stored at 4 ºC until the samples were colorimetrically analyzed for P on a Technicon Autoanalyzer II segmented flow automated colorimetry system.

A $CaCl_2$ extraction was conducted in all soil samples to extract soil nitrate and sulfate according to the procedure by Houba et al. (2000). Air-dry soil (<2 mm particle size) was extracted with a solution of 0.01 *M* $CaCl_2$ at 20 °C. In this procedure, 20 g of soil was weighed into a 100 mL plastic container and 40 mL of the $CaCl_2$ extractant dispensed into each of the containers and then shaken horizontally in a rotary shaker at 160 RPM for 2 hrs. The extract was filtered using a VWR® # 454 filter paper into 7 dram vials and stored at 4 ºC until samples were analyzed for nitrate (NO_3^--N) and sulfate (SO_4^{2-}-S) content using automated colorimetry.

3.4.5 Calculations and statistical analyses

The added fertilizer nutrient (N and P) recovered in the above-ground biomass by a crop was calculated using the following formula from Mooleki et al. (2004):

$$Recovery(\%) = \frac{Crop\ N\ or\ P\ uptake\ (treated) - Crop\ N\ or\ P\ uptake\ (control)}{Fertilizer\ (N\ or\ P)\ applied} \times 100$$

The reported results are the means of the four replicates. Where needed to stabilize variances and improve normality, nutrient concentrations were transformed. Statistical analyses were conducted using SAS 9.3 (SAS Institute, 2008) program following the mixed model procedure. The mean comparisons of crop biomass yield, applied fertilizer uptake and recovery, nutrient concentration, and soil chemical properties at different biochar rates were performed using the Tukey's HSD method (p<0.05) from a standard analysis of variance technique (ANOVA).

3.5. Results

3.5.1 Effects of biochar application on crop biomass yield

The effects of different biochar types (0, 1, 2 t ha ^{1} application rates) with standard N and P fertilization rate (100 kg N ha^{-1} and 25 kg P_2O_5 ha^{-1}) on crop above ground biomass yield (g pot^{-1}) of canola and wheat on CB-Brown and CLC-Black soil is shown in Fig. 3.2. Yield data for other biochar treatments (biochar plus 50 kg N ha^{-1} and 25 kg P_2O_5 ha^{-1}) are provided in Appendix A. Application of biochar had variable effects on canola biomass yield while the wheat grown in rotation following the canola did not show any response to biochar addition except FSB-fine biochar. Occasional reductions in crop biomass yield were observed in both crops for both soils. For the canola crop, the overall highest biomass yield was found in canola grown on the CLC-Black soils amended with WSB-Chunky (slow pyrolysis) biochar. The lowest overall biomass yield was noted for canola grown in CB-Brown soils amended with FSB-Fine (fast pyrolysis) biochar. In most of the cases, wheat grown in rotation did not show any significant (p>0.05) response to treatments with biochar alone (Fig. 3.2).

Application of biochar increased crop biomass compared to the control for all fast pyrolysis process produced biochar types (WSB-Fine and FSB-Fine) in the CLC-Black soils. For the CLC-Black soil, WSB-Fine 1 t ha^{-1} treatment had a higher yield (1.42 g pot^{-1}) than the control (0.92 g pot^{-1}). The FSB-Fine biochar applied at 2 t ha^{-1} increased canola biomass yield (1.07 g pot^{-1}) compared to control (0.76 g pot^{-1}). For wheat grown in rotation following the canola, only FSB-Fine biochar (1 t ha^{-1} rate) increased biomass yield compared to control (Fig. 3.2).

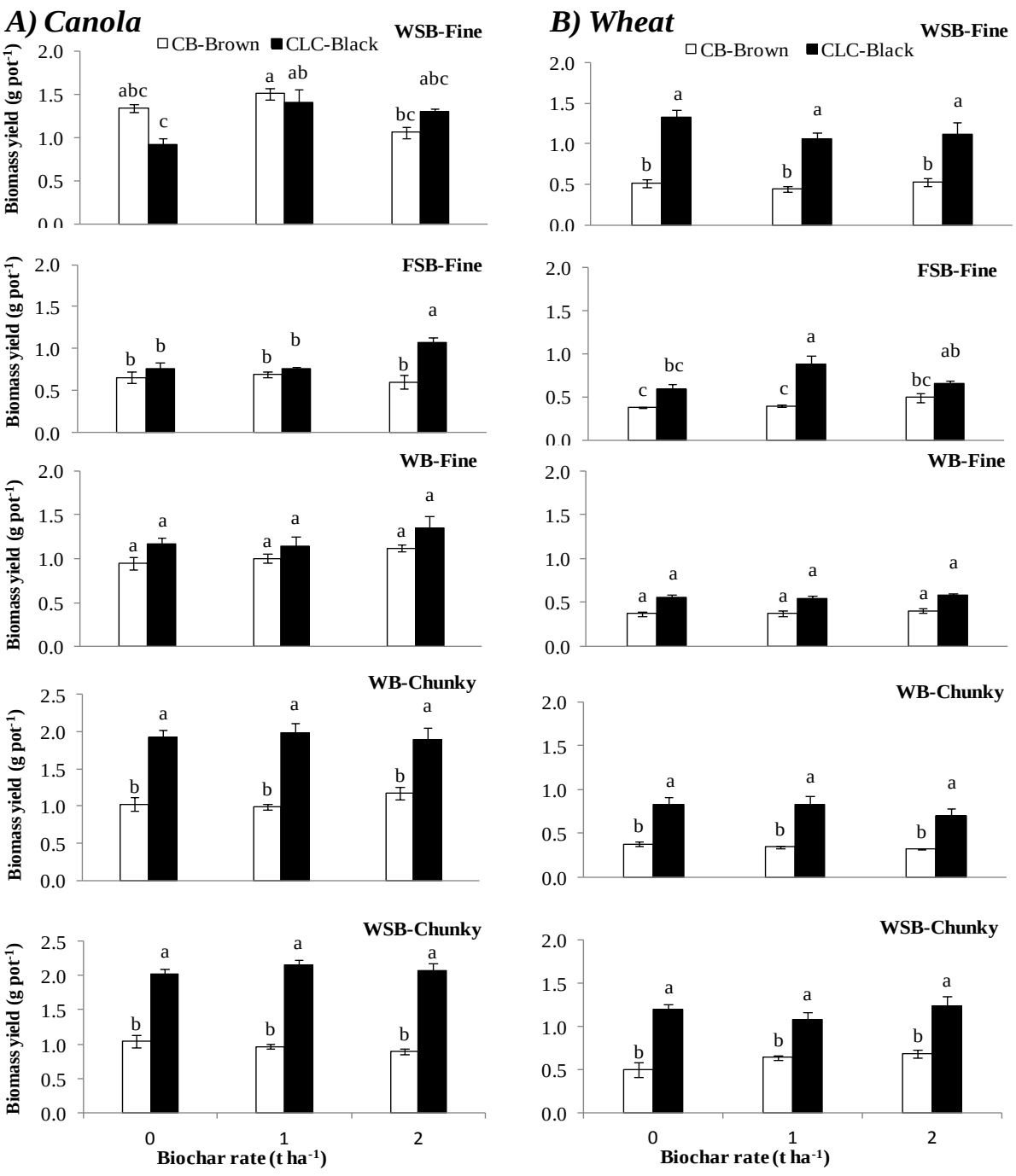

Fig. 3.2. Mean biomass yield (g pot^{-1}) of canola followed by wheat in rotation in biochar amended CB-Brown and CLC-Black soil. All treatments have 100 kg N ha^{-1} and 25 kg P_2O_5 ha^{-1} added. Error bars are standard error of mean (soil x biochar rate) with N = 24 and n = 4. (WSB-Fine = Wheat straw fine fraction fast pyrolysis biochar; FSB-Fine = Flax straw fine fraction fast pyrolysis biochar; WB-Fine = Willow fine fraction slow pyrolysis biochar; WB-Chunky = Willow chunky fraction slow pyrolysis biochar; and FSB-Chunky = Wheat straw chunky fraction slow pyrolysis biochar). For a crop and biochar type, means with different letters are significantly different (Tukey's HSD, p<0.05)

3.5.2 Effects of biochar application on fertilizer uptake and recovery

3.5.2.1 Effects on crop nitrogen and phosphorus uptake

Total N and P concentrations were determined in all plant samples collected and multiplied by biomass dry matter yield to calculate total N and P uptake (mg pot^{-1}) as shown in Table 3.3 and 3.4 respectively. All treatments had a basal fertilizer application of 100 kg N ha^{-1} and 25 kg P_2O_5 ha^{-1}. Biochar addition to the CB-Brown soil did not affect canola and wheat N uptake for any of the biochar types evaluated. Canola grown in the biochar amended CLC-Black soil always showed higher mean N uptake over the controls (Table 3.3). Wheat grown in rotation following canola in the CB-Brown soils had lowest N-uptake for all biochar types. Biochar amendment had no significant effect on N uptake by wheat for any of the biochar types on the two soils. In majority of cases P uptake was lower for wheat compared to canola (Table 3.4). The only significant effect on P uptake as influenced by biochar amendment was with canola for the WB-Fine biochar on the CB-Brown soil and for the two chunky biochars on the CLC-Black soil, where biochar amendment increased canola P uptake compared to the control.

3.5.2.2 Effects on crop nitrogen and phosphorus fertilizer recovery

The percent recovery of N and P fertilizer by canola and wheat grown in rotation was calculated for all biochar types added to the two soils (Table 3.5 and Table 3.6). Biochar addition to the CLC-Black soil generally enhanced N fertilizer recovery by canola but did not affect recovery by wheat in either of the two soils (Table 3.5). Significant enhancement of P fertilizer recovery with added biochar was observed in the CLC-Black soil, but unlike N, the recovery of fertilizer P was also increased in the willow biochar amended treatments in the CB-Brown soil (Table 3.6). As for N, no significant (p>0.05) effects of treatment were observed in the wheat crop.

Table 3.3. Nitrogen uptake (mg pot^{-1}) by canola and wheat grown in rotation in biochar amended CB-Brown and CLC-Black soil.

Biochar type†	CANOLA							WHEAT					
	CB-Brown soil‡			CLC-Black soil‡				CB-Brown soil			CLC-Black soil		
	Biochar (t ha^{-1})			Biochar (t ha^{-1})				Biochar (t ha^{-1})			Biochar (t ha^{-1})		
	0	1	2	0	1	2		0	1	2	0	1	2
	mg												
WSB-Fine	21.7 b§	25.0 ab	19.5 b	**22.2 b**	**29.0 a**	**25.5 ab**		3.8 a	4.2a	4.9a	10.5a	12.5a	13.8a
FSB-Fine	12.2 b	13.1 b	14.0 b	**15.3 b**	**13.2 b**	**21.3 a**		4.2 c	4.0 c	4.4 bc	8.3 a	7.7 a	7.6 ab
WB-Fine	15.9 b	16.9 b	17.7 ab	22 ab	22.1 ab	24.5 a		3.8 b	4.1 b	3.8 b	7.6 a	7.8 a	10.3 a
WB-Chunky	7.3 c	9.3 c	10.9 c	**26.2 b**	**31.7 a**	**35.4 a**		3.6 b	3.3 b	3.1 b	8.0 a	8.3 a	8.1 a
WSB-Chunky	8.2 c	13.9 c	15.5 c	**31.4 b**	**40.3 a**	**43.4 a**		3.7 b	3.7 b	4.6 b	9.8 a	8.9 a	8.1 a
ANOVA		**F**	***p***		**SEM¶**				**F**	***p***		**SEM**	
WSB-Fine													
Soil x Biochar rate		2.07	0.155		1.351				0.10	0.910		1.758	
FSB-Fine													
Soil x Biochar rate		3.96	0.038		1.305				0.19	0.826		0.728	
WB-Fine													
Soil x Biochar rate		0.13	0.878		1.656				3.04	0.073		0.634	
WB-Chunky													
Soil x Biochar rate		2.87	0.083		1.178				0.41	0.672		0.375	
WSB-Chunky													
Soil x Biochar rate		0.98	0.394		1.722				3.81	0.042		0.483	

† WSB-Fine = Wheat straw fine fraction fast pyrolysis biochar; FSB-Fine = Flax straw fine fraction fast pyrolysis biochar; WB-Fine = Willow fine fraction slow pyrolysis biochar; WB-Chunky = Willow chunky fraction slow pyrolysis biochar; and FSB-Chunky = Wheat straw chunky fraction slow pyrolysis biochar

‡ All treatments received 100 kg N ha^{-1} as urea and 25 kg P_2O_5 monoammonium phosphate

§ For a crop, means (soil x biochar rate) with the same letter in the same row are not significantly different (p<0.05) (N = 24, n = 4). The multi-treatment comparisons were made using the Tukey's HSD method

¶ Standard error of mean

Table 3.4. Phosphorus uptake (mg pot^{-1}) by canola and wheat grown in rotation in biochar amended CB-Brown and CLC-Black soil

Biochar type†	CANOLA						WHEAT					
	CB-Brown soil‡			CLC-Black soil‡			CB-Brown soil			CLC-Black soil		
	Biochar (t ha^{-1})			Biochar (t ha^{-1})			Biochar (t ha^{-1})			Biochar (t ha^{-1})		
	0	1	2	0	1	2	0	1	2	0	1	2
	mg											
WSB-Fine	3.8 a§	4.2 a	3.7 a	2.0 b	2.6 b	2.6 b	0.5 b	0.4 b	0.5 b	1.6 a	1.3 a	1.3 a
FSB-Fine	1.8 a	1.8 a	1.9 a	1.5 a	1.8 a	2.0 a	0.4 b	0.4 b	0.5 ab	0.5 ab	0.8 a	0.5 ab
WB-Fine	**1.9 b**	2.4 ab	**2.7 a**	2.0 b	1.9 b	2.1 ab	0.5 b	0.4 b	0.5 b	0.6 ab	0.7 a	0.6 ab
WB-Chunky	2.7 ab	3.2 a	3.2 a	**2.3 b**	**3.4 a**	**3.5 a**	0.8 ab	1.0 a	0.7 ab	0.5 b	0.5 b	0.5 b
WSB-Chunky	2.9 b	3.2 b	3.3 b	**3.2 b**	**3.5 ab**	**4.4 a**	1 .0 d	1.2 bcd	1.1 cd	1.7 a	1.5 abc	1.6 ab
ANOVA		**F**	***p***		**SEM¶**			**F**	***p***		**SEM**	
WSB-Fine												
Soil x Biochar rate		3.26	0.062		0.142			1.48	0.254		0.103	
FSB-Fine												
Soil x Biochar rate		1.21	0.323		0.136			4.26	0.031		0.072	
WB-Fine												
Soil x Biochar rate		3.18	0.066		0.146			4.63	0.024		0.042	
WB-Chunky												
Soil x Biochar rate		1.94	0.172		0.204			1.12	0.349		0.085	
WSB-Chunky												
Soil x Biochar rate		2.23	0.136		0.214			1.73	0.205		0.108	

† WSB-Fine = Wheat straw fine fraction fast pyrolysis biochar; FSB-Fine = Flax straw fine fraction fast pyrolysis biochar; WB-Fine = Willow fine fraction slow pyrolysis biochar; WB-Chunky = Willow chunky fraction slow pyrolysis biochar; and FSB-Chunky = Wheat straw chunky fraction slow pyrolysis biochar

‡ All treatments received 100 kg N ha^{-1} as urea and 25 kg P_2O_5 monoammonium phosphate

§ For a crop, means (soil x biochar rate) with the same letter in the same row are not significantly different (p<0.05) (N = 24, n = 4). The multi-treatment comparisons were made using the Tukey's HSD method

¶ Standard error of mean

Table 3.5. Recovery of applied nitrogen fertilizer by canola and wheat grown in rotation in biochar amended CB-Brown and CLC-Black soil

Biochar type†	CANOLA							WHEAT					
	CB-Brown soil‡			CLC-Black soil‡				CB-Brown soil			CLC-Black soil		
	Biochar (t ha^{-1})			Biochar (t ha^{-1})				Biochar (t ha^{-1})			Biochar (t ha^{-1})		
	0	1	2	0	1	2		0	1	2	0	1	2
	----------			----------			%	----------			----------		
WSB-Fine	36.5 abc§	43.2ab	32.7 bc	28.3 c	**48.2 a**	36.3 abc		0.4 b	0.6 b	2.3 ab	7.6 ab	9.5 ab	13.8 b
FSB-Fine	17.5 b	20.3 b	21.9 ab	19.4 b	18.1 b	**31.4 a**		4.5 a	4.4 a	4.6 a	3.7 a	4.3 a	4.1 a
WB-Fine	23.8 a	27.5 a	30.5 a	29.7 a	33.4 a	38.8 a		2.5 b	3.1 ab	2.7 b	5.4 ab	5 ab	7.7 a
WB-Chunky	11.3 c	16.4 c	19.1 bc	28.9 b	**43.7 a**	**49.3 a**		1.8 b	1.8 b	1.2 b	4.8 ab	4.4 ab	6.7 a
WSB-Chunky	11.9 c	25.7 bc	27 bc	35.5 b	**56.9 a**	**53.8 a**		- 0.3 b	3.7 ab	4.1 ab	8.0 a	7.4 a	5.4 a
ANOVA		**F**	***p***		**SEM¶**				**F**	***p***		**SEM**	
WSB-Fine													
Soil x Biochar rate		2.37	0.122		3.332				0.29	0.749		2.855	
FSB-Fine													
Soil x Biochar rate		3.14	0.068		2.386				0.03	0.974		1.387	
WB-Fine													
Soil x Biochar rate		0.08	0.926		3.534				1.01	0.385		1.123	
WB-Chunky													
Soil x Biochar rate		4.17	0.032		2.285				1.38	0.277		0.962	
WSB-Chunky													
Soil x Biochar rate		0.54	0.594		3.680				4.56	0.025		1.177	

† WSB-Fine = Wheat straw fine fraction fast pyrolysis biochar; FSB-Fine = Flax straw fine fraction fast pyrolysis biochar; WB-Fine = Willow fine fraction slow pyrolysis biochar; WB-Chunky = Willow chunky fraction slow pyrolysis biochar; and FSB-Chunky = Wheat straw chunky fraction slow pyrolysis biochar

‡ All treatments received 100 kg N ha^{-1} as urea and 25 kg P_2O_5 monoammonium phosphate

§ For a crop, means (soil x biochar rate) with the same letter in the same row are not significantly different (p<0.05) (N = 24, n = 4). The multi-treatment comparisons were made using the Tukey's HSD method

¶ Standard error of mean

Table 3.6. Recovery of applied phosphorus fertilizer by canola and wheat grown in rotation in biochar amended CB-Brown and CLC-Black soil

Biochar type†	CANOLA							WHEAT					
	CB-Brown soil‡			CLC-Black soil‡				CB-Brown Soil			CLC-Black soil		
	Biochar (t ha^{-1})			Biochar (t ha^{-1})				Biochar (t ha^{-1})			Biochar (t ha^{-1})		
	0	1	2	0	1	2		0	1	2	0	1	2
							%						
WSB-Fine	13.9 ab§	17 a	14.8 a	8.7 b	12.4 ab	13.9 ab		0.3 ab	-0.1 b	0 ab	3.3 a	1.7 ab	2.2 ab
FSB-Fine	3.5 a	4.6 a	4.7 a	3.4 a	8.5 a	6.4 a		1 a	1.1 a	1.8 a	1.2 a	2.2 a	1.1 a
WB-Fine	**5.4 b**	9.1 ab	**12.2 a**	7 ab	8.1 ab	7.7 ab		0.7 a	0.8 a	1.6 a	1.9 a	1.8 a	1.8 a
WB-Chunky	**5.0 c**	**16.6 ab**	9.5 bc	**7.0 c**	**20.9 a**	**18.7 a**		2.8 a	1 a	0.3 a	0.9 a	0.7 a	1.9 a
WSB-Chunky	6.3 b	12.4 ab	12.5 ab	**11.6 b**	**15.1 ab**	**21.4 a**		- 0.5 b	2.8 ab	0 b	5.2 a	1.7 ab	2.1ab
ANOVA		**F**	***p***		**SEM¶**				**F**	***p***		**SEM**	
WSB-Fine													
Soil x Biochar rate		1.51	0.249		1.326				0.38	0.689		0.749	
FSB-Fine													
Soil x Biochar rate		1.04	0.375		1.386				0.90	0.425		0.635	
WB-Fine													
Soil x Biochar rate		2.69	0.095		1.322				1.09	0.356		0.397	
WB-Chunky													
Soil x Biochar rate		2.56	0.105		1.624				1.61	0.226		0.959	
WSB-Chunky													
Soil x Biochar rate		1.16	0.335		2.079				4.66	0.023		1.123	

† WSB-Fine = Wheat straw fine fraction fast pyrolysis biochar; FSB-Fine = Flax straw fine fraction fast pyrolysis biochar; WB-Fine = Willow fine fraction slow pyrolysis biochar; WB-Chunky = Willow chunky fraction slow pyrolysis biochar; and FSB-Chunky = Wheat straw chunky fraction slow pyrolysis biochar

‡ All treatments received 100 kg N ha^{-1} as urea and 25 kg P_2O_5 monoammonium phosphate

§ For a crop, means (soil x biochar rate) with the same letter in the same row are not significantly different (p<0.05) (N = 24, n = 4). The multi-treatment comparisons were made using the Tukey's HSD method

¶ Standard error of mean

3.5.3 Effects of biochar application on soil nutrient concentrations and chemical properties

3.5.3.1 Biochar effects on soil nutrient concentrations

Soil sampling for analysis of residual nutrient concentration was completed at the end of the rotation following wheat harvest. Soil samples were analyzed for available soil NO_3^--N, PO_4^+-P and SO_4^{2-}-S concentrations. The residual soil nitrate concentrations were low and not significantly (p>0.05) different among biochar rates or soil (Table 3.7).

Extractable available soil phosphate concentrations were similar among biochar rates for a soil (Table 3.8). The CB-Brown soil generally had higher phosphate concentration than the CLC-Black soil, consistent with differences observed at the beginning of the experiment (Table 3.1). . The content of residual available phosphorus in the CB-Brown soil was significantly (p<0.05) increased by the application of two biochar types (FSB-Fine and WB Chunky (Table 3.8) and may be related to the higher P content of these two biochars (Table 3.2). All the biochar types did not greatly affect residual extractable sulfate concentrations in both soils. Residual extractable sulfate values were relatively low, ranging from about 2 to 5 mg SO_4^{2-}-S kg^{-1} (data not shown).

3.5.3.2 Biochar effects on soil chemical properties

Soil from the pots collected following wheat harvest at the end of the experiment was analyzed for soil pH, electrical conductivity (salinity) and percent organic carbon (% OC). Biochar amendment in the two soils had little effect on soil pH (Table 3.9). The only effect was observed in the CLC-Black soil amended with FSB-Fine biochar (2 t ha^{-1}) that had significantly (p<0.05) higher pH over the control, but was only 0.2 pH units higher and of little biological significance. Lack of large liming type effect is explained by low rates of amendment and the highly buffered nature of the two soils. Biochar amendment in the both soils had no effect on soil EC (data not shown) likely due to the low rates of added char. The EC values in all treatments were all below 1 ds m^{-1} and considered non-saline.

The highest rates of biochar amendment produced the highest mean SOC concentrations (Table 3.10). However, the differences were not significant and are explained by the low rate (2 t ha^{-1}) of biochar application. NO_3^--N

Table 3.7. Soil extractable nitrate concentration (mg NO_3^--N kg^{-1}) in biochar amended CB-Brown and CLC-Black soil

Biochar type†	**CB-Brown soil**‡			**CLC-Black soil**‡		
	Biochar (t ha^{-1})			Biochar (t ha^{-1})		
	0	1	2	0	1	2
WSB-Fine	1.8 ab§	1.5 ab	3.2 a	2.2 ab	1.2 b	1.5 ab
FSB-Fine	5.6 a	7.7 a	3.2 a	1.8 a	1.8 a	1.5 a
WB-Fine	2.0 a	2.2 a	4.5 a	2.4 a	2.3 a	6.5 a
WB-Chunky	1.2 b	0.1 b	0.5 b	1.7 ab	1.7 ab	3.4 a
WSB-Chunky	**1.8 b**	**3.3 a**	2.6 ab	3.4 a	2.5 ab	2.8 a
ANOVA		**F**	***p***		**SEM**¶	
WSB-Fine						
Soil x Biochar rate		3.060	0.072		0.426	
FSB-Fine						
Soil x Biochar rate		1.360	0.282		4.074	
WB-Fine						
Soil x Biochar rate		0.330	0.721		1.284	
WB-Chunky						
Soil x Biochar rate		3.240	0.063		0.473	
WSB-Chunky						
Soil x Biochar rate		16.98	0.001		0.212	

† WSB-Fine = Wheat straw fine fraction fast pyrolysis biochar; FSB-Fine = Flax straw fine fraction fast pyrolysis biochar; WB-Fine = Willow fine fraction slow pyrolysis biochar; WB-Chunky = Willow chunky fraction slow pyrolysis biochar; and FSB-Chunky = Wheat straw chunky fraction slow pyrolysis biochar

‡ All treatments received 100 kg N ha^{-1} as urea and 25 kg P_2O_5 monoammonium phosphate

§ Means (soil x biochar rate) with the same letter in the same row are not significantly different (p<0.05) (N = 12, n = 4). The multi-treatment comparisons were made using the Tukey's HSD method

¶ Standard error of mean

Table 3.8. Soil extractable phosphorus concentrations (mg PO_4^+-P kg^{-1}) in biochar amended CB-Brown and CLC-Black soil

Biochar type†	**CB-Brown soil**‡			**CLC-Black soil**‡		
	Biochar (t ha^{-1})			Biochar (t ha^{-1})		
	0	1	2	0	1	2
WSB-Fine	14.7 a§	14 a	15.5 a	9.5 b	9.3 b	8.2 b
FSB-Fine	**14.3 b**	**16.3 ab**	**18.1a**	10.4 c	10.9 c	11.3 c
WB-Fine	13.8 ab	12.8 ab	14.5 a	10.9 b	11.1 b	12.0 ab
WB-Chunky	**17.9 b**	**20.5 a**	**19.1 ab**	7.2 c	5.6 c	6.0 c
WSB-Chunky	18.2 a	22.5 a	19.6 a	7.4 b	6.9 b	6.3 b
ANOVA		**F**	***p***		**SEM**¶	
WSB-Fine						
Soil x Biochar rate		6.54	0.007		0.387	
FSB-Fine						
Soil x Biochar rate		0.38	0.687		0.739	
WB-Fine						
Soil x Biochar rate		0.46	0.641		0.664	
WB-Chunky						
Soil x Biochar rate		7.69	0.004		0.542	
WSB-Chunky						
Soil x Biochar rate		2.44	0.115		1.087	

† WSB-Fine = Wheat straw fine fraction fast pyrolysis biochar; FSB-Fine = Flax straw fine fraction fast pyrolysis biochar; WB-Fine = Willow fine fraction slow pyrolysis biochar; WB-Chunky = Willow chunky fraction slow pyrolysis biochar; and FSB-Chunky = Wheat straw chunky fraction slow pyrolysis biochar

‡ All treatments received 100 kg N ha^{-1} as urea and 25 kg P_2O_5 monoammonium phosphate

§ Means (soil x biochar rate) with the same letter in the same row are not significantly different (p<0.05) (N = 12, n = 4). The multi-treatment comparisons were made using the Tukey's HSD method

¶ Standard error of mean

Table 3.9. Soil pH in CB-Brown and CLC-Black soil ameded with different biochars

Biochar type‡	pH†					
	CB-Brown soil§			CLC-Black soil§		
	Biochar (t ha^{-1})			Biochar (t ha^{-1})		
	0	1	2	0	1	2
WSB-Fine	8.0 a¶	8.0 a	8.0 a	6.6 b	6.6 b	6.7 b
FSB-Fine	7.9 a	7.9 a	7.9 a	**6.6 c**	**6.6 c**	**6.8 b**
WB-Fine	7.9 a	7.9 a	7.9 a	6.6 b	6.6 b	6.6 b
WB-Chunky	7.9 a	7.9 a	7.8 a	6.6 b	6.6 b	6.6 b
WSB-Chunky	7.9 a	7.9 a	8.0 a	6.4 b	6.5 b	6.4 b
ANOVA		**F**	***p***		**SEM#**	
WSB-Fine						
Soil x Biochar rate		0.45	0.646		0.021	
FSB-Fine						
Soil x Biochar rate		2.30	0.129		0.039	
WB-Fine						
Soil x Biochar rate		13.37	0.081		0.021	
WB-Chunky						
Soil x Biochar rate		0.71	0.504		0.022	
WSB-Chunky						
Soil x Biochar rate		3.16	0.067		0.027	

† pH of a 1:2 (soil:water) extract

‡ WSB-Fine = Wheat straw fine fraction fast pyrolysis biochar; FSB-Fine = Flax straw fine fraction fast pyrolysis biochar; WB-Fine = Willow fine fraction slow pyrolysis biochar; WB-Chunky = Willow chunky fraction slow pyrolysis biochar; and FSB-Chunky = Wheat straw chunky fraction slow pyrolysis biochar

§ All treatments received 100 kg N ha^{-1} as urea and 25 kg P_2O_5 monoammonium phosphate

¶ Means (soil x biochar rate) with the same letter in the same row are not significantly different (p<0.05) (N = 12, n = 4). The multi-treatment comparisons were made using the Tukey's HSD method

Standard error of mean

Table 3.10. Soil organic carbon (% OC) in CB-Brown and CLC-Black soil ameded with different biochars

Biochar type†	OC (%)					
	CB-Brown soil‡			CLC-Black soil‡		
	Biochar (t ha^{-1})			Biochar (t ha^{-1})		
	0	1	2	0	1	2
WSB-Fine	1.5 b§	1.6 b	1.6 b	4.5 a	4.6 a	4.6 a
FSB-Fine	1.7 b	1.6 b	1.8 b	4.9 a	4.7 a	5.0 a
WB-Fine	1.6 b	1.7 b	1.7 b	4.4 a	4.5 a	4.6 a
WB-Chunky	2.1 b	2.2 b	2.2 b	4.3 a	4.4 a	4.5 a
WSB-Chunky	2.1 b	2.2 b	2.2 b	4.4 a	4.4 a	4.6 a
ANOVA		**F**	***p***		**SEM¶**	
WSB-Fine						
Soil x Biochar rate		0.01	0.994		0.094	
FSB-Fine						
Soil x Biochar rate		1.01	0.384		0.074	
WB-Fine						
Soil x Biochar rate		0.57	0.576		0.059	
WB-Chunky						
Soil x Biochar rate		2.26	0.133		0.049	
WSB-Chunky						
Soil x Biochar rate		1.80	0.194		0.058	

† WSB-Fine = Wheat straw fine fraction fast pyrolysis biochar; FSB-Fine = Flax straw fine fraction fast pyrolysis biochar; WB-Fine = Willow fine fraction slow pyrolysis biochar; WB-Chunky = Willow chunky fraction slow pyrolysis biochar; and FSB-Chunky = Wheat straw chunky fraction slow pyrolysis biochar

‡ All treatments received 100 kg N ha^{-1} as urea and 25 kg P_2O_5 monoammonium phosphate

§ Means (soil x biochar rate) with the same letter in the same row are not significantly different (p<0.05) (N = 12, n = 4). The multi-treatment comparisons were made using the Tukey's HSD method

¶ Standard error of mean.

3.6 Discussion

3.6.1 Effects of biochar application on crop biomass yield

The results obtained in this controlled environment study indicate that different sources of biochar performed differently in affecting yield in a canola-wheat rotation. Evidence of yield enhancement was found in the fast pyrolysis wheat and flax straw fine biochar amendments. Biochar application to soils is reported to increase yield of crops grown on the biochar amended soils (Lehmann and Joseph, 2009; Woolf et al., 2010; Spokas et al., 2012) in controlled environments as well as in the field (Lehmann and Rondon, 2006; Chan et al., 2007; Asai et al., 2009; Chan and Xu, 2009; Kloss et al., 2013). In agreement with the findings of these researchers and other, the effect is dependent on the soil and biochar type.

In our experiment, the CLC-Black Chernozem soil, characterised by higher SOM content, appeared more responsive in yield to biochar amendment than CB-Brown Chernozem soils, despite the fact that the soil nutrient contents were relatively similar in both soils. This higher SOM content may result in greater ability to compensate for any N immobilization induced by biochar. Also, as the pH of the CLC-Black soil is lower to begin with, any increases in alkalinity from the char may be more beneficial in this soil. Lentz and Ippolito (2012) applied hardwood-derived alkaline biochar (22.4 t ha^{-1}) to a calcareous soil with pH 7.7 and found that biochar did not alter pH or availability of $P0_4$-P and cations, as is typically observed for acidic soils. They also suggested that biochar applications to calcareous soils may lead to reduced N availability, requiring additional soil N inputs to maintain target yields. Residual effects of the char after the first crop (canola) were limited. In the case of the wheat, lack of yield response to biochar is likely at least partly a consequence of most available nutrients being taken up by canola as a first crop with little left available for wheat. The wheat crop did exhibit considerable signs of N and P deficiency throughout the growing period. There was no evidence of any direct toxic effects from the char in the form of reduced germination or emergence. Occasionally however, lower mean crop biomass yields in biochar amended soils suggest some potential for reduced nutrient availability and uptake.

Biochar is suggested to cause N immobilization and could potentially cause N deficiency in plants when applied to soil due to high C: N ratio (Chan and Xu, 2009; Lehmann and Joseph, 2009). Organic amendments with available C: N ratios above 20 are known to cause microbial N

immobilization (Fisher and Binkley, 2000). However, the availability of biochar C for microbial decomposition and assimilation in the biochars used in this study is not known. Previous studies (e.g., Alotaibi, 2014) that have examined CO_2 release in biochar amended prairie soils have shown the biochar to be highly resistant to decomposition. The total C and N content in biochar does not reflect the actual availability to microbes to cause immobilization. Gajić and Koch (2012) who worked with a German Luvisol amended with 10 t ha^{-1} of hydrochar suggested that hydrochar can decrease plant available N due to N immobilization. Lentz and Ippolito (2012) applied hardwood biochar to an Aridisol at 22 t ha^{-1} and found no effect on corn silage yield in the first year, but observed a 36 % yield decrease in the second year and concluded that the suppression in yield was due either to reduced nutrient (N, S, Mn, and Cu) availability or nutrient uptake. The response observed by Lentz and Ippolito (2012) was similar to an effect observed in low organic C-containing soils by Zimmerman et al. (2011) where the biochar may have induced a reduction in soil C mineralization, which in turn limited at least soil N and S availability.

Spokas et al. (2012), in their biochar review article, reported that biochar application rates in research studies have ranged from <1 to over 100 t ha^{-1}, and reported relative response to biochar compared to controls from negative 50 % to positive yield increases ~200 %. Such great variation likely stems from the large range of biochar application rates, crops, and soil types used. In this study, two fast pyrolysis fine biochars produced from crop sources (WSB-Fine and FSB-Fine) resulted in significant yield increases at higher rates when applied to the CLC-Black soil. In the same soil, the FSB-Fine biochar also had a significant positive residual effect on wheat biomass yield. These two biochars added at a rate of 2 t ha^{-1} would add approximately 20 kg N ha^{-1}, 30 kg P_20_5 ha^{-1}, and 3 kg S ha^{-1}. However, only a small portion of this nutrient would likely be plant available (Stefankiw, 2012). These two biochars also had the greatest CEC, but the effect on total soil CEC would likely be small when only 2 t ha^{-1} of char is added. Still, with biochar addition, greater N uptake along with greater N fertilizer recovery implies enhanced availability of N in soil amended with biochar. Enhanced CEC in the slightly acidic CLC-Black through a biochar type effect resulting in a slight increase in pH may increase N availability by reducing leaching and denitrification losses. Chan et al. (2008) in a pot trial in the greenhouse added poultry litter biochar at rate of 10 and 50 t ha^{-1} to an Alfisol and recorded a yield increase 42 and 96 % over the control which was largely attributed to the ability of biochars to increase N availability in this soil.

3.6.2 Effects of biochar application on fertilizer uptake and recovery

Biochar addition to the CB-Brown soil did not significantly (p>0.05) affect canola and wheat N uptake and recovery for all biochar types. However, canola grown in biochar amended CLC-Black soils typically showed greater N uptake and % recovery compared to the unamended controls. The increased nutrient uptake in CLC-Black soils by both wheat straw biochars was associated with an increase in biomass nutrient concentrations. Since wheat was grown in rotation as the second crop, greater uptake by canola would deplete the available nutrient for the subsequent wheat crop. Consequently, most biochar types failed to produce a residual impact on the wheat.

Usually, soil amended with biochar is found to have greater nutrient retention than unamended soils (Ding et al., 2010). One probable mechanism reported by most literature is related to enhancing CEC of soils and hence, enhanced nutrient retention (Tryon, 1948; Mbagwu and Piccolo, 1997; Lehmann et al., 2003; Liang et al., 2006; Joseph et al., 2010; Laird et al., 2010). In this study, the effect seems most pronounced in the CLC-Black soil. Kammann et al. (2012) added peanut hull biochar at 50 t ha^{-1} to a German Luvisol and then grew ryegrass and observed a significantly reduced N loss from denitrification, and associated greater N uptake by plants grown in the presence of biochar. In contrast, Schnell et al. (2012) applied up to 3 t ha^{-1} of sorghum [*Sorghum bicolor* (L.) Moench] biochar to an Alfisol and then grew sorghum for 45 d and concluded that low nutrient uptake and recovery in plants grown in biochar-treated soil could have contributed to a lack of yield response but they did not explain the mechanisms behind the low nutrient recovery. An assessment of N losses from leaching and denitrification as affected by biochar addition would be recommended for future research. A few instances of enhanced fertilizer P recovery by canola with biochar addition were observed in this study on both soils. The mechanism for this is not known, but could be related to reduce P fixation on the solid phase, enhanced root growth, and beneficial conditions in the rhizosphere.

3.6.3 Effects of biochar on residual soil nutrient concentrations and chemical properties

3.6.3.1 Effects on soil nutrient concentrations

Biochar can play a key role in nutrient cycling, potentially affecting nutrient retention and availability when applied to soils. In our study, soil extractable NO_3^--N, PO_4^+-P, and SO_4^--S concentrations remaining in both soils at the end of the experiments were found to be largely unaffected by biochar addition, except for extractable PO_4^+-P in the FSB-Fine and WSB-Fine biochar treatments in the CB-Brown soil. Higher residual soil P contents are consistent with enhanced P availability in these treatments as they also showed significantly increased recovery of fertilizer P compared to the controls. Biochar may supply a source of plant-available nutrients once applied to the soil (Gaskin et al., 2008; Sohi et al., 2010) but this was not observed in this study where biochars were added without added N and P fertilizer. Brewer et al. (2012) amended a semi-arid sandy Mollisol with 10 t ha^{-1} biochar made under various pyrolysis conditions and generally observed an increase in soil extractable P, and K compared with unamended soil. Sinclair et al. (2010) in a field study on a ferrosol amended a soil with manure biochar and reported an increase in available P. However, the same soil amended with greenwaste biochar did not show an increase in available P. In contrast, high rates of biochar application (4.4 % and 11 %, w/w) to a sandy yellow earth resulted in a small but statistically significant reduction in available P (Van Zwieten et al., 2010b). Therefore, small and variable effects of biochars on soil available N and P status may be expected, as observed in this study.

3.6.3.2 Effects on soil chemical properties

Most biochar is alkaline in nature and therefore, can directly alter soil pH. Since biochar typically has higher pH than soil it can act as a liming agent, resulting in an overall increase in soil pH (Glaser et al., 2002; Lehmann and Rondon, 2006). In our study, biochar types did not increase in soil pH except for one case in the CLC-Black soil. Increasing the pH of an acid soil increases nutrient availability and decreases the proportion of Al^{3+} and H^+ ions occupying cation exchange sites, which effectively increases base saturation (Brady and Weil, 2004). The starting pH of the CLC-Black soil was the lower of the two tested soils, with a value of 6.5; whereas most biochar had a pH around 9 and above. The CB-Brown soil had an initial pH (8) that was

close to the pH of the biochar, which would explain why there was no change in pH relative to untreated soil following biochar addition. The pH of both soils did not change following biochar addition, possibly because of the low biochar rates used and that both soils were already highly buffered by relatively high clay and SOC content (McCauley, 2009; McElligott et al., 2011).

Biochar amendment in both soils had little effect on soil EC and % OC; likely due to the low rates of added char. Biochars are suggested to have long residence times in many ecosystems (Agee, 1996; Lehmann et al., 2006; Mann, 2008). A trend towards increased SOC concentrations does point towards a C sequestration effect in these two soils, one that may only be detectable at biochar application rates much greater than what was used in the current study.

3.7 Conclusion

The results of this experiment with five different biochars added at two rates to two contrasting Saskatchewan soils under controlled environment conditions showed that the effect of biochar application on crop yield, nutrient recovery, and soil properties is dependent on soil type and was found to differ among the biochar types. Biochar addition tended to increase canola biomass yield and nutrient recovery on the Black Chernozem, a soil with higher OM but lower pH than the Brown Chernozem, where fewer significant effects were observed. Fast pyrolysis fine biochars with high CEC appeared more effective in promoting canola growth and nutrient uptake than chunky ones. Wheat grown after canola showed little response to biochar amendment, likely as a result of nutrient depletion by the preceding canola crop. In both soils, biochar did not greatly alter residual soil extractable nutrient content, and had no effect on EC or % OC concentrations. Chapter 4 evaluates the effects of the amendments on the two soils under actual field conditions.

4. Effect of Biochar on Crop Yield, Nutrient Uptake and Recovery, Soil Nutrients, and Moisture Use Efficiency by Canola-Wheat Grown in Rotation in a Brown And Black Chernozem in the Field

4.1 Preface

In Chapter 3, the effects of biochar on crop growth and soil properties in two Chernozem soils, along with the nutrient uptake and recovery, and growth of canola and wheat were evaluated under controlled environment conditions. The experiment showed that despite biochar addition at rates of 1-2 t ha^{-1} to two cultivated prairie Chernozem soils differing in organic matter (OM) content, biochar applications did not have large effects on soil properties or plant growth when grown under optimum conditions of moisture and temperature in the growth chamber. Therefore, field studies were undertaken to examine responses under variable environmental situations in actual field conditions (Chapter 4). In experiments under field conditions, I seek to represent the real conditions faced by the farmer, and document the responses under variable environmental conditions of the two soils in their actual field setting.

4.2 Abstract

Carbon (C) rich biochars have often proven effective in highly weathered tropical soils. However, less is known about how biochars behave as amendments when added to temperate prairie soils. Previously, most studies used high biochar rates (tens to hundred t ha^{-1}), but such high rates are impractical for farm application. Moreover, information on impacts of different biochars produced from different feedstocks and under different pyrolysis conditions is inadequate. Therefore, a study was conducted to evaluate the response of canola-wheat grown in rotation to four different biochars added to a Brown and Black Chernozem soil in a field site experiment. Biochars were obtained from locally available sources. Treatments were biochar added at 1 and 2 t ha^{-1} without and with nitrogen (N) and phosphorus (P) fertilizers

at 50 or 100 kg N ha^{-1} and 25 kg P_2O_5 ha^{-1}. Parameters evaluated were crop biomass and grain yield, N and P uptake, % recovery of applied N and P, residual soil nutrients (NO_3^--N, and PO_4^+-P), pH, electrical conductivity (EC), % organic carbon (% OC) and soil moisture. Application of biochar was found to have variable effects on canola yield while the subsequent wheat crop did not show any response to biochar amendment except wheat straw fine fraction biochar. Application of biochar resulted in significant increases (p<0.05) in canola and wheat grain yield for the wheat straw fine fraction biochar only when added to Black Chernozem. Occasional depressions in crop biomass yield were observed for both crops with both soils. In agreement with the growth chamber studies (Chapter 3), the results of the field site experiment show that despite additional mineral fertilization, short-term growth inhibition may occur when applying some biochars to temperate prairie soils. However, no significant biochar and fertilizer interaction was observed. In these calcareous Chernozems, biochar did not greatly alter the availability of N and P, and its effects on soil pH, % OC, EC, and soil moisture content were often non-significant. We suggest that biochar applications at 1-2 t ha^{-1} to prairie Chernozems will not have large effects on soil properties or plant growth when grown in a field site experiment.

4.3 Introduction

Biochar refers to black Carbon (BC) which is a C rich, predominantly stable, organic C compound that is produced when biomass (e.g., agricultural crop residues, wood, waste, etc.) is heated through the process of pyrolysis in an oxygen-depleted environment (Verheijen et al., 2010). Human beings started using BC since fire pits were built on soil by early human civilization (Lefroy, 1883; Spokas et al., 2012). It has been established that soils without high amounts of BC are significantly less fertile than soils that contain BC. An example of this increased soil fertility is the "Terra Preta" soils of central Amazonia, which are presumably human-made by pre-Columbian native populations (Kleiner, 2009). Terra Preta soils have, on average, three times higher soil organic matter (SOM) content, higher nutrient levels and a better nutrient retention capacity than surrounding infertile soils (Glaser et al., 2001). Soil amendment with biochar has attracted extensive attention in the late 1980's because it increases the C sequestration in soils (Kwapinski et al., 2010) and thereby decreases the amounts of CO_2 that entering the atmosphere (Lehmann, 2007a; Lehmann, 2007b; Novak et al., 2009, Kwapinski et

al., 2010). Commonly measured quality parameters of biochar include OC content, ash content, nutrient content, elemental composition, surface area, porosity, surface functional groups, cation exchange capacity (CEC), and sorption properties (Gaskin et al., 2009). In pyrolysis of biochar, most of the calcium (Ca), magnesium (Mg), potassium (K), phosphorus (P), plant micronutrients, and about half of the N and sulfur (S) in the biomass feedstock are partitioned into the biochar fraction (Laird et al., 2010). As a result, use of biochar as a soil amendment returns most of the nutrients back to the soils. Biochar also increases the capacity of soils to adsorb plant nutrients (Lehman et al., 2007a; Cheng et al., 2008; Spokas et al., 2012), thereby reducing nutrient leaching losses. Biochar has been shown to decrease soil bulk density, increase CEC, and nutrient cycling, and the ability of soils to retain plant available water. Therefore, the use of biochar as a soil amendment is expected to increase both nutrient and water use efficiency, thereby agronomic crop productivity (Glaser et al., 2001; Liang et al., 2006). Several reports indicate that soil biochar applications alters soil properties and increase crop yields (Lehman, 2007a; Chan et al., 2008; Spokas et al., 2012). Much of this work on the impact of biochar on soil quality and agronomic yield has been conducted in the highly weathered Oxisols and Ultisols of the tropics that intrinsically have low nutrient retention capacity. By contrast, temperate soils of northern Great Plains are typically dominated by higher levels of SOM, greater CEC, greater nutrient content and water holding capacities. Hence, the impact of biochar on a prairie Chernozem soils is likely to be different from tropical soils and needs to be investigated.

The use of growth chambers allows the control and maintenance of certain environmental conditions (e.g., light, temperature, and moisture), and thus enables easier quantification of the treatment effects, without external interferences. On the other hand, in experiments under field conditions, we seek to represent the real situations faced by farmers, and document the treatment effects of treatment on soil properties and plant performance under actual environmental conditions experienced in the field. Therefore, the general objective of this study was to evaluate the effectiveness of different biochars as soil amendments to improve soil conditions for crop growth, with emphasis on soil fertility impacts under field situations in variable environmental conditions. Two sites were chosen for the study to provide a contrast in soil properties and provide representation of the southern and northern agricultural regions of Saskatchewan. The specific objectives were to investigate the effects of amendment with four different biochars

applied at two rates on canola (*Brassica napus*) and wheat (*Triticum aestivum*) biomass yield, uptake and % recovery of applied N and P under field conditions at two contrasting Saskatchewan field sites; and to evaluate the effect of biochars on soil properties, including available nutrients, SOC, pH and EC at the end of each growing season.

4.4 Materials and methods

4.4.1 Study site and biochar production

Experimental plots were established in fall 2011 on two sites at two different locations in the agricultural region of Saskatchewan, Canada (Fig. 4.1). The Brown Chernozem site is located on a farm about 5 km southeast of Central Butte, Saskatchewan, Canada (legal location SW31-20-3-3) in the southern mixed grass prairie region. The soils in this area are dominated by Orthic Brown Chernozems (Aridic Borolls). The field research site is classified as a mixture of Kettlehut and Ardill soil associations. The Kettlehut soil association is predominantly a Brown Solod to a Brown Solodized Solonetz, and the Ardill soil association is dominantly an Orthic Brown to a Calcareous Brown Chernozem (Soil Classification Working Group 1998). The actual soils of the treatment plots is Ardill association. The parent material is moderately fine textured, moderately calcareous, glacial till with a loam soil texture.

The Black Chernozem site is located at the Conservation Learning Center (CLC) research farm, about 18 km south of Prince Albert (legal location SE20-46-26-W2), Saskatchewan, Canada. It features rolling topography, wetlands and remnant native upland areas. The actual research site is an Orthic Black Chernozem, Meota association (Typic Cryoboroll) of clay loam texture, on a gently sloping topography. Both the soil and landscape are typical of the region in the northern agricultural region of Saskatchewan. Lehmann (2007a) stated that the addition of C as biochar is likely to have more benefit in a soil with low OM content than high OM content. Therefore, the Brown Chernozem site of Central Butte, Saskatchewan (CB-Brown) with low OC content (1.5 %) and the Black Chernozem site of CLC farm near Prince Albert, Saskatchewan (CLC-Black) with relatively higher OC content (2.7 %) provide a good contrast in SOC contents for the study.

A total of four biochars were obtained from three different feedstock sources: wheat straw (*Triticum aestivum* L.), flax straw (*Linum usitatissimum* L.), and willow stems (*Salix spp.)*

The three different feedstocks were used to produce four different biochars. Among the four biochars tested, Saskatchewan Research Council (Saskatoon, SK, Canada) provided fast pyrolysis wheat straw fine fraction biochar (WSB-Fine) and fast pyrolysis flax straw fine fraction biochar (FSB-Fine). They also supplied slow pyrolysis willow fine fraction biochar (WB-Fine), and slow pyrolysis willow chunky fraction biochar (WB-Chunky). In the fast pyrolysis process, the reactor temperature was ~ 400 °C with residence time less than 1 min, whereas for slow pyrolysis the reactor temperature varied between 300 to 600 °C with residence time less than 60 min.

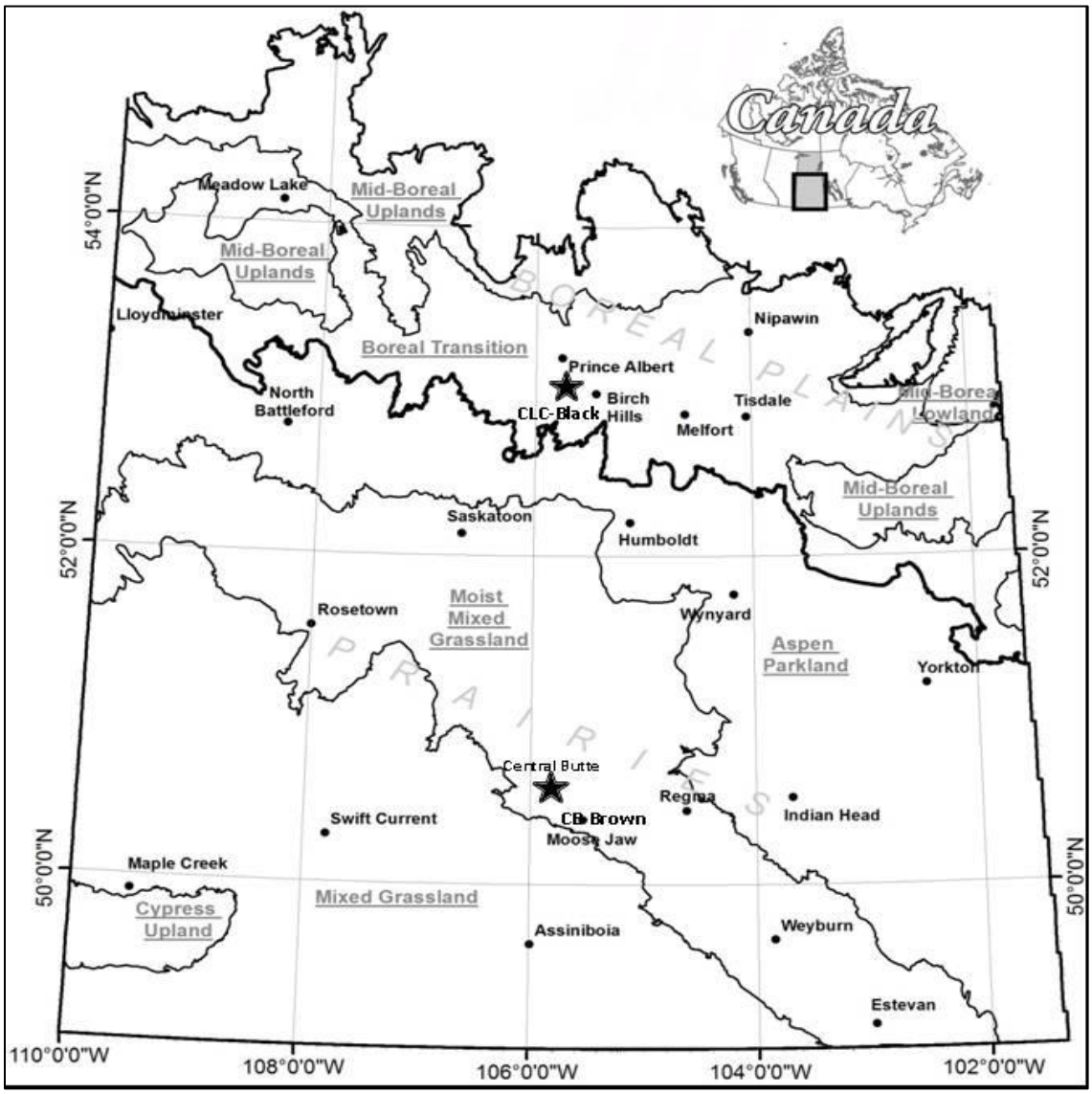

Fig. 4.1. Locations of two study sites in Saskatchewan, Canada. ArcGIS10 (Environmental Systems Research Institute, Inc., Redlands, CA, USA) map courtesy of Dr. Beyhan Amichev

The CB-Brown soil is of sandy loam texture and relatively low in extractable NO_3^--N and NH_4^+-N content with low EC and moisture content. On the other hand, the CLC-Black soil is clay-loam in texture with greater NO_3^--N and NH_4^+-N content and higher EC and moisture content. Initially, both soils show moderate contents of extractable available PO_4^+-P. The CB-Brown soil is especially low in OC. The pH of CB-Brown soil is neutral to slightly basic and the CLC-Black soil is slightly basic. Electrical Conductivity is low (rated as non-saline) in both soils.

4.4.2 Soil and biochar characterization and meteorological data

In the early spring of 2012, initial soil sampling was done and basic soil characteristics were measured and are summarized in Table 4.1.

Table 4.1. Initial soil properties of the study site

Parameters	**CB-Brown soil**		**CLC-Black soil**	
	Mineral soil depth (cm)		Mineral soil depth (cm)	
	0-30	30-60	0-30	30-60
NO_3^--N (kg ha^{-1})†	16.2	4.7	39.9	26.3
NH_4^+-N (kg ha^{-1})†	12.4	20.3	25.6	31.9
PO_4^+-P (kgha^{-1})†	25.6	nd‡	25.3	nd
% OC	1.2	nd	2.7	nd
pH§	7.5	nd	7.9	nd
EC (ds m^{-1})¶	0.25	nd	0.64	nd
Moisture (%)#	14.2	15.7	27.1	31.1
Soil texture††	Sandy loam		Clay loam	
Sand (%)	61.8	nd	40.0	nd
Silt (%)	23.8	nd	32.2	nd
Clay (%)	14.3	nd	27.9	nd

† Extractable NO_3^--N, NH_4^+-N and PO_4^+-P
‡ nd = Not determined
§ pH of a 1:2 (soil:water) extract
¶ EC (electrical conductivity of a 1:2 (soil:water) extract
# Moisture (%) by weight at time of sampling
†† Soil textures were determined using USDA texture triangle

Air dried biochar samples were analyzed and their properties are summarized in Table 4.2. All biochars had pH>7 and are considered alkaline. The least alkaline was the fast

pyrolysis FSB-Fine biochar (pH 8.6) while the most alkaline was the slow pyrolysis WB-Fine biochar (pH 10.3). The two fast pyrolysis biochars (WSB-Fine and FSB-Fine) had similar CEC values (36 and 32 Cmol kg^{-1} while the slow pyrolysis WB-Fine was highest (54 Cmol kg^{-1}). The slow pyrolysis WB-Chunky had the lowest CEC. Specific Surface Area (SSA) was determined with the N_2 adsorption method according to Brunauer et al. (1938). The fast pyrolysis biochars had similar SSA's (1.03-3.02 m^2 g^{-1}) while the values for WB-Fine and WB-Chunky were approximately two orders of magnitude greater.

Table 4.2. Physical and chemical characteristics of different biochars

Parameters	Biochar type†			
	WSB-Fine	**FSB-Fine**	**WB-Fine**	**WB-Chunky**
Pyrolysis process	Fast	Fast	Slow	Slow
SSA‡ (m^2 g^{-1})	2.4	1.0	238.4	175.0
pH (H_2O)	9.2	8.6	10.3	9.7
VM§ (%)	24.1	29.7	15.5	12.8
TOC (%)	68	73	62	84
CEC (Cmol kg^{-1})	36	32	54	11
Ash (%)	15	8	25	11
TN¶ (%)	0.9	1.4	1.1	0.7
P_2O_5# (%)	2.4	6.2	2.7	4.0
TS†† (%)	0.15	0.14	0.08	0.04

† WSB-Fine = Wheat straw fine fraction fast pyrolysis biochar; FSB-Fine = Flax straw fine fraction fast pyrolysis biochar; WB-Fine = Willow fine fraction slow pyrolysis biochar; WB-Chunky = Willow chunky fraction slow pyrolysis biochar; and WSB-Chunky = Wheat straw chunky fraction slow pyrolysis biochar

‡ Specific surface area; air-dried samples were analyzed by Pore Science Labs, Bristol, PA; and measured based on Brunauer–Emmett–Teller (BET) –N_2 adsorption. For others, by Loring Laboratories, Calgary, Alberta

§ Volatile Organic Matter

¶ Total Nitogen

In Ash

†† Total Sulphur

The daily mean temperature and precipitation for the study period (2012 and 2013) including the 30-year long-term average of both CB-Brown and CLC-Black sites is reported in Table 4.3. Both sites showed similar temperature regimes throughout the growing season except April, 2013 in which the observed daily mean temperature was shown to be cooler for both sites than the long term averages. The CLC-Black site was observed to have higher mean precipitation

for all months than CB-Brown site. Historically, the lowest mean precipitation is observed in April and highest in June-July for both sites. The monthly precipitation in 2012 was higher than the long-term average for the first three months of the growing season at both sites, and this trend continued until September for the CLC-Black site. In 2013, the early part of the growing season (April-May) at both sites was drier than normal, becoming wetter later in the season. At the CLC-Black site in 2012, wet spring conditions and frost interfered with crop emergence and growth.

Table 4.3. General weather data for the two study sites. Data from closest Environment Canada meteorological stations: Elbow for CB-Brown and Prince Albert for CB-Black

Site	Year	Months					
		April	May	June	July	August	September
		Daily mean temperature (°C)					
CB-Brown	2012	10.7	10.2	15.2	18.9	17.5	12.6
	2013	-1.0	12.0	14.1	16.5	17.8	16.0
	30-year Average†	4.9	11.0	15.8	18.7	17.8	11.9
CLC-Black	2012	3.5	10.4	16.0	20.2	17.6	12.3
	2013	-1.9	12.6	15.6	17.1	17.2	13.3
	30-year Average	3.1	10.3	15.1	17.7	16.3	10.3
		Total precipitation (mm)					
CB-Brown	2012	33.8	115.5	109.1	37.4	26.1	4.1
	2013	6.2	28.7	82.0	54.4	59.8	41.8
	30-year Average	19.8	47.4	65.4	56.1	39.8	33.9
CLC-Black	2012	47.6	77.0	110.8	103.6	78.4	22.6
	2013	22.4	11.8	181.6	89.6	20.0	20.2
	30-year Average	26.9	43.7	71.3	73.1	61.8	43.0

† 30 years Average of daily mean

4.4.3 Experimental design, setup, and sampling

Field plot trials were conducted at both experimental sites (CB-Brown and CLC-Black) to evaluate the performance of the biochars in field sites as a function of biochar application rate and type on plant yield and N and P and recovery. The field plot trials began in 2012 at both sites. The sites are the same general locations from which soils were taken for the growth

chamber studies (Chapter 3). There were four different biochar types tested at both sites, rather than the five used in the growth chamber study (Chapter 3) as there was not sufficient amounts of the WSB-Chunky biochar used in growth chamber studies for application in the field.

Biochars were added to the soils of both sites (CB-Brown and CLC-Black) in April of 2012. The biochars were applied by hand on a calm day as the powdery, ashy nature of the chars made them very difficult to uniformly apply in the field. The experiment at each site was designed as a split-split plot design with three biochar application rates (0, 1 and 2 t ha^{-1}) alone and in combination with 50 (low rate) or 100 (standard or typical rate) kg N ha^{-1} as urea (46-0-0) and 25 (typical rate) kg P_2O_5 ha^{-1} as mono ammonium phosphate (12-51-0). The rates of biochar were selected as rates that could be practically applied in the field, as quantities of biochar larger than about 2 t ha^{-1} tended to remain on the surface even after incorporation, and were subsequently redistributed by wind and seeding equipment. The total number of main plots per site was 18 with an individual plot size of 2×2 m. Small plot size was necessitated by the limited quantities of biochar available for field application and the need to apply the char by hand. Fertilizer combinations were applied to the main plot areas. Each main plot was then divided into 3 subplots where biochar rates were applied. The biochar types were applied to the split-split plots. The numbers of replications were 4 and the replicates were set up as 4 blocks of replicate treatments. Therefore the total number of main plots were 72 (18×4) and the total number of split plots were 288 (72×4). All four biochars were tested in each plot.

Prior to the experiment, both experimental sites were cropped with field pea (*Pisum sativum)* in 2011. After harvest, the fields were tilled to a depth of 10-12 cm. In the first year of the experiment, on April 23, 2012, fertilizer treatment was broadcasted on the main plots of CB-Brown experimental plots and biochar treatments were hand applied to the designated split-plots of the CB-Brown experiment. Immediately after treatment application, all plots were rototilled to a depth of 15 cm. On May 04, plots of the CB-Brown site were sprayed with glyphosphate at a rate of 0.8 L ha^{-1} to kill weeds. On the following day on May 05, 2012, the plots were seeded with canola (*Brassica napus* var. LL 5770*)* at a rate of 5 kg ha^{-1} using an air seeder with 30 cm row spacing and at a depth of approximately 2 cm using direct seeding method. We applied glufosinate herbicide to the same plots on June, 07, 2012 to control further weed infestation that had emerged, at which time, the canola was in the cotyledon stage. The canola from CB-Brown sites was harvested on August 13, 2012.

At the CLC-Black site, the treatments were added to the designated plots on May 09, 2012. Fertilizer treatments were broadcasted on the main plots and biochar treatments were hand applied to the designated split-plots. Immediately after treatment application, all plots were rototilled to a depth of 15 cm. On May 10, plots were sprayed with glyphosphate at a rate of 0.8 L ha^{-1} to kill weeds. On the following day on May 11, 2012, the plots were seeded with canola (*Brassica napus* var. Nexerra 1012 RR*)* at a rate of 6 kg ha^{-1} using a Hege cone seeder with 20 cm row spacing and at a depth of approximately 2 cm using direct seeding method. The canola from CLC-Black sites was harvested on September 26, 2012.

After the canola was harvest, both fields were cultivated to a depth of 10-12 cm using a field cultivator with sweeps. In 2013, wheat was grown as the rotational crop following canola on both experimental sites. No further fertilization or biochar amendment was done. On May 19, 2013, the plots of CB-Brown sites were seeded with wheat (*Triticum aestivum* var. Waskeda hard red spring wheat) at a rate of 80 kg ha^{-1} using an air seeder with 30 cm row spacing and at a depth of approximately 2 cm using direct seeding method. The crop was sprayed with fluoxypyr, 2,4-D, fenoxyprop tank mix herbicide on June 17, 2013 to control weed infestation that had emerged. The wheat crop from CB-Brown sites was harvested on August 19, 2013. The CLC-Black sites was seeded with wheat (*Triticum aestivum* var. Field Star spring wheat*)* on May 26, 2013, at a rate of 100 kg ha^{-1} using a Hege cone seeder with 20 cm row spacing and at a depth of approximately 2 cm using direct seeding method. The crop was sprayed with florasulam mixed with glyphosate herbicide on May 20, 2013 to control weed infestation. The wheat crop from CLC-Black sites was harvested on September 4, 2013.

Canola and wheat were hand harvested from each plot at maturity and were dried, weighed for dry matter yield, threshed to separate grain from straw, and grain weight recorded. Both grain and straw sub samples were taken and ground for further analysis for above-ground crop N and P uptake. Soil samples were collected from all subplots in the spring of 2012 and 2013, and in the fall (after crop harvest) of 2012 and 2013 from both sites and subsequently frozen at a temperature of -18 °C. Soil samples were collected at a depth of 0-30 cm and 30-60 cm, for soil residual available N and P content and at a depth of 0-15 cm for SOC content. A sub-sample was taken from each sample and used for gravimetric moisture measurement. After collecting, all samples were mixed thoroughly to provide a composite sample for each

subplot. All composite soil samples were then air-dried, ground to pass a 2-mm sieve and stored at room temperature for laboratory analysis.

4.4.4 Soil and plant analyses

Initial soil characteristics of the two sites were determined in a sub-sample of the soil collected from the field following drying and homogenization. Soil texture was determined by a laser scattering particle size distribution analyzer (HORIBA© LTD., 2007). Electrical conductivity and pH were measured by the glass electrode method using 1: 2 soil: water suspension (Nelson and Sommers, 1982). Soil organic carbon was measured using the Leco C632 carbon combustion analyzer (LECO© Corporation, 2007).

Total N and P in all straw and grain samples were determined by standard H_2SO_4-H_2O_2 digestion as described by Thomas et al. (1967). For these measurements, 0.25 g of sample was weighed into 75 mL digestion tubes, 5 mL of concentrated H_2SO_4 was added in each digestion tube, and this suspension was heated at 360 °C for 30 min and then allowed to cool. This was repeated five times. The N and P in the extracts were measured using a Technicon Autoanalyzer II segmented flow automated colorimetry system.

The Modified Kelowna (MK) extractions were conducted in all soil samples according to the procedure by Qian et al. (1994). The extractant was prepared by combining 28 mL of 0.25 *M* acetic acid, 38.5 g of 0.25 *M* ammonium acetate, and 1.11 g of 0.015 *M* ammonium fluoride into a 2 L volumetric flask. Soil samples (3 g) was weighed into 100 mL plastic containers, and 30 mL of the MK extracting solution was dispensed into each of the containers and then shaken horizontally in a rotary shaker at 160 RPM for 5 min. The extract was filtered using a VWR® # 454 filter paper into 7 Dram vials and stored at 4 ºC until the samples were colorimetrically analyzed for P on a Technicon Autoanalyzer II segmented flow automated colorimetry system.

A KCl extraction was conducted on all soil samples to extract soil NO_3^- and NH_4^+ according to the procedure by Maynard and Kalra (1993). Air-dry soil (<2-mm particle size) was extracted with a solution of 2.0 M KCl at 20 °C. In this procedure, 5 g of soil was weighed into a 100 mL plastic container and 50 mL of the KCl extractant dispensed into each of the containers and then shaken horizontally in a rotary shaker at 160 RPM for 30 min. The extract was filtered

using VWR® # 454 filter paper into 7 dram vials and stored at 4 °C until samples were analyzed for nitrate (NO_3^--N) and ammonium (NH_4^+-N) content using automated colorimetry. A representative sub-sample (approximately 10 g) for gravimetric moisture determination was then placed on a metal tray, and oven dried for 24 hrs at a temperature of 100 ± 5 °C to determine soil moisture content.

4.4.5 Calculations and statistical analyses

The added fertilizer nutrient (N and P) recovered in the above-ground biomass by a crop was calculated using the following equation 1, from Mooleki et al. (2004):

$$Recovery(\%) = \frac{Crop\ N\ or\ P\ uptake\ (treated) - Crop\ N\ or\ P\ uptake\ (control)}{Fertilizer\ (N\ or\ P) applied} \times 100 \ldots\ldots\ldots\ldots (1)$$

Water use efficiency was calculated using yield produced per unit of stored soil moisture plus precipitation by following the equation 2 and 3.

$$Mass\ of\ water\ (in\ sample) = Wet\ mass - Dry\ mass \ldots\ldots (2)$$

$$Moisture\ (\%) = \frac{Mass\ of\ water}{Dry\ mass\ of\ sample} \times 100 \ldots\ldots\ldots (3)$$

The reported results are the means of the four replicates. Where needed to stabilize variances and improve normality, nutrient concentration data were transformed. Statistical analyses were conducted using SAS 9.3 (SAS Institute, 2008) program following the mixed model procedure. The mean comparisons of crop biomass yield, applied fertilizer uptake and recovery, nutrient concentration and soil chemical properties at different biochar rates were performed using the Tukey's HSD method ($P \leq 0.05$) from a standard analysis of variance technique (ANOVA). We also included more powerful, single-degree-of-freedom contrast tests in the ANOVA analyses. These tested the effect of individual amendments rates on yield, compared biochar rates (biochar 1 t ha^{-1}, biochar 2 t ha^{-1} or biochar average of 1 t ha^{-1} + 2 t ha^{-1} as a class vs. no biochar treatments (control, no biochar).

4.5 Results

The early to midspring (end of April and until mid-May) time period was unusually cool during both years of the study, along with high precipitation especially in 2012 (Table-4.3). In 2012, early May was the coldest at the CLC-Black site, along with high precipitation. Thus in 2012, canola emergence and seedling establishment was delayed relative to more typical growing seasons. Canola did not emerge or very poor emergence was recorded in some blocks of CLC-Black sites due to excess precipitation and freezing soil temperatures (below -3°C) after seeding in May, 2012.

4.5.1 Effects of biochar application on crop biomass and grain yield

The ANOVA indicated that biochar type plus biochar rate, and fertilizer treatment interactions were non-significant ($p>0.05$) for CB-Brown site for both canola and wheat for both total biomass and grain biomass (Table 4.4). For CLC-Black site, fertilizer treatment, biochar rate, and biochar rate plus fertilizer treatment interactions were found significant ($p<0.05$) for biomass yield and grain biomass by both canola and wheat. In the first year, the fertilizer treatments were found to have significant ($p<0.05$) differences between treatments for both total biomass and grain biomass at both sites (Table 4.4).

In CLC-Black site, biochar types were found significant for canola and biochar rate was found to be significant for wheat total biomass and grain biomass. Biochar rates did not show any class contrast effects on CB-Brown site. On the other hand, the biochar rates of 0 t ha^{-1} and 2 t ha^{-1} were shown to have significant differences in class contrast for both crops grown on CLC-Black soil.

Table 4.4. The influence of biochar and fertilizer treatments and their interactions on crop above ground total biomass and grain biomass for both experimental sites

Sources of Variation	CB-Brown				CLC Black			
	Total biomass		Grain biomass		Total biomass		Grain biomass	
	F†	*P*†	F	*P*	F	*P*	F	*P*
	1st Year: Canola‡							
Biochar type (BT)	1.6	0.184	2.6	0.055	4.2	**0.007**	12.7	**<0.001**
Biochar rate (BR)	0.8	0.433	0.9	0.393	2.9	0.060	10.2	**<0.001**
Fert. Treat. (FT)§	32.6	**0.001**	34.7	**0.001**	30.8	**0.001**	24.4	**<0.001**
BR × FT¶	1.1	0.337	1.6	0.104	3.4	**0.011**	4.8	**0.001**
BR × BT × FT#	0.8	0.835	0.8	0.880	0.9	0.618	1.1	0.371
Contrast††								
BR 0 vs (1+2)tha^{-1}	0.9	0.337	0.1	0.744	5.6	**0.020**	0.1	0.762
BR 0 vs 1 t ha^{-1}	1.6	0.206	0.9	0.344	3.3	0.073	6.3	**0.014**
BR 0 vs 2 t ha^{-1}	0.2	0.690	0.2	0.703	5.2	**0.025**	4.0	**0.049**
	2nd Year: Wheat‡‡							
Biochar type (BT)	0.3	0.813	0.5	0.689	1.0	0.406	1.0	0.415
Biochar rate (BR)	0.3	0.746	0.5	0.626	6.7	**0.002**	7.7	**0.001**
Fert. Treat. (FT)	0.6	0.725	1.0	0.393	9.5	**0.001**	8.5	**<0.001**
BR × FT	1.1	0.346	1.2	0.289	3.0	**0.022**	3.4	**0.012**
BR × BT × FT	0.6	0.986	0.6	0.980	0.7	0.835	0.8	0.765
Contrast								
BR 0 vs (1+2)tha^{-1}	0.0	0.994	0.1	0.803	2.5	0.118	3.3	0.074
BR 0 vs 1 t ha^{-1}	0.1	0.708	0.1	0.803	0.1	0.782	0.0	0.855
BR 0 vs 2 t ha^{-1}	0.2	0.698	0.5	0.495	9.1	**0.003**	10.9	**0.001**

† P and F values for treatment effects and interaction terms and single-degree-of-freedom orthogonal comparison derived from an ANOVA (p<0.05)

‡ 1st Year (2012) canola grown in the first year as a first crop of the rotation

§ Fertilizer treatment (FT)

¶ Biochar rate (BR) and Fertilizer treatment (FT) interactions

Biochar rate (BR), Biochar types (BT) and Fertilizer treatment (FT) interactions

†† Orthogonal contrast = Classes compared biochar rates (biochar 1 t ha^{-1}, biochar 2 t ha^{-1}, or biochar average of 1 t ha^{-1} + 2 t ha^{-1}) as a class vs. no biochar treatments (control, no biochar)

‡‡ 2nd Year (2013) wheat grown in the second year as a second crop of the rotation

The effects of different biochar types (0, 1, 2 t ha^{-1} application rates) with combination of N and P fertilization on crop grain yield (t ha^{-1}) of canola and wheat grown on CB-Brown and CLC-Black soil is shown in Fig. 4.2 and 4.3. Total above ground biomass yield data are provided in Appendix B. Application of biochar had no effects on canola and wheat grown in rotation on CBBrown site while CLC-Black sites showed variable effects on canola and wheat grain yield. Occasional reductions in grain biomass yield were observed in both crops at both study sites. For the canola crop, the overall highest biomass yield was found in canola grown on the CB-Brown sites amended with WSB-fine (fast pyrolysis) biochar. The lowest overall biomass yield was noted for canola grown in CLC-Black soils amended with WB-Fine (slow pyrolysis) biochar. In most of the cases, wheat grown in rotation did not show any significant response to treatments with biochar alone except for WSB-fine (fast pyrolysis) biochar at the CLC-Black site (Fig. 4.2).

Application of biochar produced significant ($p<0.05$) increases in canola crop grain yield compared to the control for all fast pyrolysis process produced biochar types (WSB-Fine and FSB-Fine) in the CLC-Black soils. For the CLC-Black soil, WSB-Fine 2 t ha^{-1} treatment had a significantly higher canola grain yield (2.13 t ha^{-1}) than the control (1.30 t ha^{-1}). For wheat grown in rotation following the canola, only WSB-Fine biochar (2 t ha^{-1} rate) produced a significant increase in biomass yield compared to 1 t ha^{-1} applied in the CLC-Black soil (Fig. 4.3).

4.5.2 Effects of biochar application on fertilizer uptake and recovery

4.5.2.1 Effects on crop nitrogen and phosphorus uptake

Total N and P concentrations were determined in all straw and grain samples collected and multiplied by the respective straw and grain biomass yield to calculate above-ground total N and P uptake (kg ha^{-1}), as shown in Table 4.5 and 4.6 respectively.

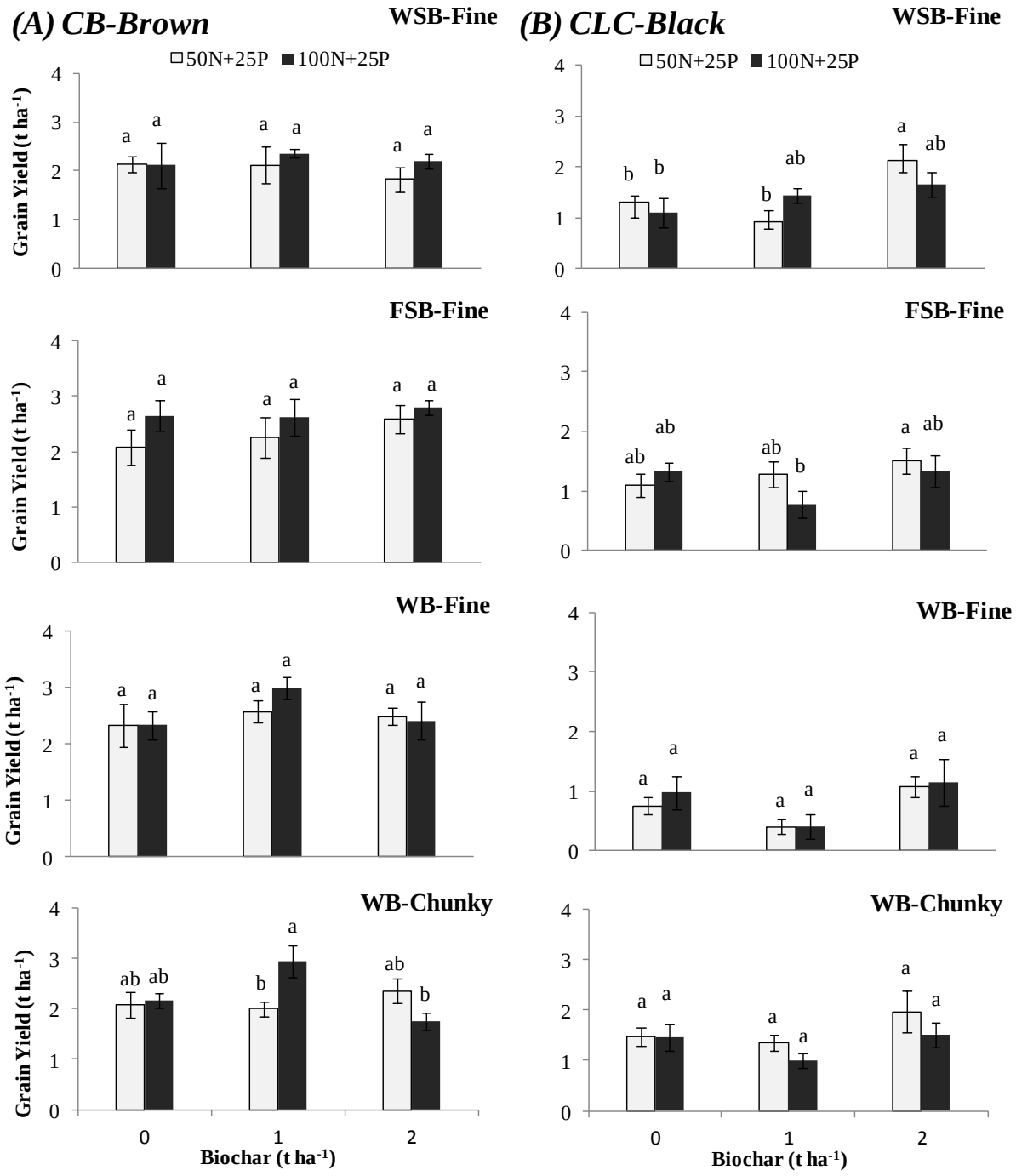

Fig. 4.2. Mean grain yield (t ha^{-1}) of canola grown in the first year as a first crop in a rotation in biochar amended (A) CB-Brown and (B) CLC-Black soil. Error bars are standard error of mean (biochar rate x fertilizer treatment) with N = 24 and n = 4. (WSB-Fine = Wheat straw fine fraction fast pyrolysis biochar; FSB-Fine = Flax straw fine fraction fast pyrolysis biochar; WB-Fine = Willow fine fraction slow pyrolysis biochar; WB-Chunky = Willow chunky fraction slow pyrolysis biochar). For a soil and biochar type, means with different letters are significantly different (Tukey's HSD, p<0.05)

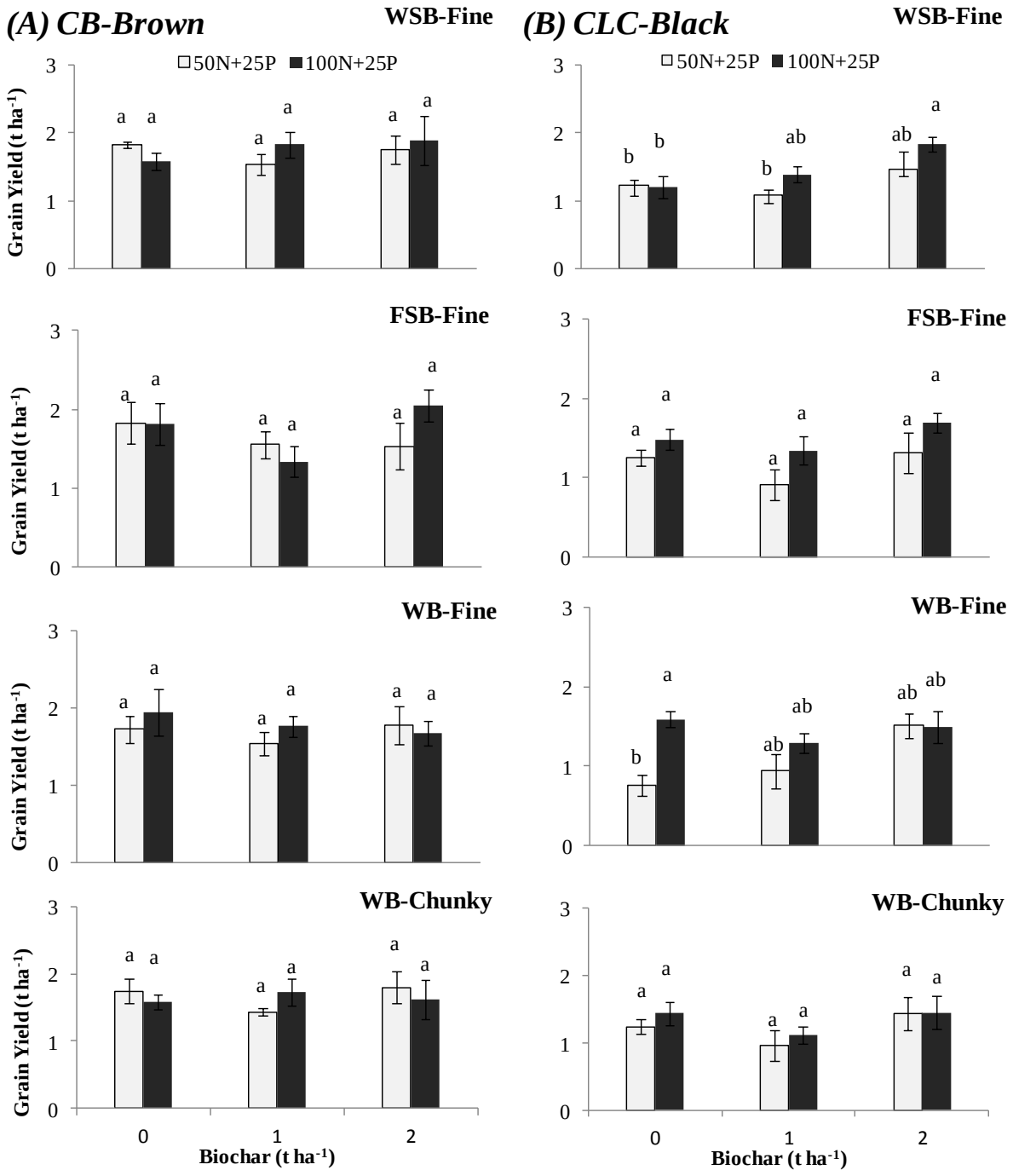

Fig. 4.3. Mean grain yield (t ha^{-1}) of wheat grown in the second year as a second crop in a rotation in biochar amended (A) CB-Brown and (B) CLC-Black soil. Error bars are standard error of mean (biochar rate x fertilizer treatment) with N = 24 and n = 4. (WSB-Fine = Wheat straw fine fraction fast pyrolysis biochar; FSB-Fine = Flax straw fine fraction fast pyrolysis biochar; WB-Fine = Willow fine fraction slow pyrolysis biochar; WB-Chunky = Willow chunky fraction slow pyrolysis biochar). For a soil and biochar type, means with different letters are significantly different (Tukey's HSD, $p<0.05$)

Biochar addition to the CB-Brown site did not affect canola N and P uptake for any of the biochar types evaluated. Occasional depression of N uptake by canola was noted at the CB-Brown site and the depression increased with increasing biochar rates. On the other hand, canola grown in the biochar amended CLC-Black site always showed higher mean N uptake over the controls (Table 4.6). Biochar amendment had some significant effect on N uptake by the biochar types on the CLC-Black soils. WSB-Fine biochar increased N uptake with increasing rate of biochar on the CLC-Black soil (Table 4.6).

Biochar amendment had no significant (p>0.05) effect on P uptake for any of the biochar types on the two soils. In majority of cases P uptake was lower in CLC-Black site compared to CB-Brown site (Table 4.5 and Table 4.6). The only significant effect on P uptake as influenced by biochar amendment was with canola for the WB-Fine biochar on the CB-Brown soil and for the two chunky biochars on the CLC-Black soil, where biochar amendment increased canola P uptake compared to the control. In most cases, the biochar types and fertilizer interactions were not significant for N and P uptake by canola at both study sites except WB-Chunky (slow pyrolysis) on the CB-Brown soils and WSB-Fine on the CLC-Black soil.

4.5.2.2 Effects on crop N and P fertilizer recovery

The N and P fertilizer recovery by canola was calculated for all biochar types added to the CB-Brown sites (Table 4.7). Due to the crop loss of some plots (loss of control plots to calculate P recovery) in CLC-Black site, P fertilizer recovery could not be calculated and only N recovery by canola was calculated for all biochar types added to the CLC-Black site (Table 4.8). There were no significant (p>0.05) effects of the biochar addition on N and P fertilizer recovery in the CB-Brown site observed. Biochar addition to both sites generally enhanced mean N fertilizer recovery by canola. Biochar type did not have an effect on N and P recovery at either site. In most cases, the biochar types and fertilizer interactions did not affect N and P recovery by canola on CB-Brown or CLC-Black sites.

Table 4.5. Nitrogen and phosphorus uptake (kg ha^{-1}) by canola grown in rotation as first crop in biochar amended CB-Brown soil

Biochar type†	N Uptake (kg ha^{-1})						P Uptake (kg ha^{-1})					
	50N+25P‡			100N+25P§			50N+25P			100N+25P		
	Biochar (t ha^{-1})			Biochar (t ha^{-1})			Biochar (t ha^{-1})			Biochar (t ha^{-1})		
	0	1	2	0	1	2	0	1	2	0	1	2
	kg ha^{-1}											
WSB-Fine	56 A a¶	68 A a	77 A a	74 A a	82 A a	75 A a	12 A a	13 A a	15 A a	15 A a	15 A a	14 A a
FSB-Fine	70 A a	77 A a	94 A a	59 A a	94 A a	102 A a	13 A a	15 A a	16 A a	14 A a	15 A a	16 A a
WB-Fine	85 A a	84 A a	83 A a	80 A a	101 A a	86 A a	15 A a	17 A a	15 A a	15 A a	17 A a	17 A a
WB-Chunky	**65 A b**	72 A ab	84 A ab	77 A ab	**101 A a**	84 A b	12 A a	14 A a	14 A a	13 A a	17 A a	13 A a
ANOVA		**F**	***p***		**SEM#**			**F**	***p***		**SEM**	
WSB-Fine (BR x FT††)		0.95	0.408		13.46			0.87	0.439		1.81	
FSB-Fine (BR x FT)		0.98	0.400		10.11			2.38	0.127		1.48	
WB-Fine (BR x FT)		1.05	0.374		9.27			0.63	0.546		1.05	
WB-Chunky (BRxFT)		6.88	**0.008**		10.07			1.75	0.207		1.48	

† WSB-Fine = Wheat straw fine fraction fast pyrolysis biochar; FSB-Fine = Flax straw fine fraction fast pyrolysis biochar; WB-Fine = Willow fine fraction slow pyrolysis biochar; and WB-Chunky = Willow chunky fraction slow pyrolysis biochar

‡ 50 kg N ha^{-1} as urea and 25 kg P_2O_5 ha^{-1} as monoammonium phosphate

§ 100 kg N ha^{-1} as urea and 25 kg P_2O_5 ha^{-1} as monoammonium phosphate

¶ For a given nutrient uptake, means (biochar type, N = 16, R = 4) with the same upper case letter in the same column and means (biochar rates x fertilizer treatment, N = 24, n = 4) with the same lower case letter in the same row are not significantly different (p<0.05). The multi-treatment comparisons were made using the Tukey's HSD method

Standard error of mean

†† Biochar rate (BR) and Fertilizer treatment (FT) interaction

Table 4.6. Nitrogen and phosphorus uptake (kg ha^{-1}) by canola grown in rotation as first crop in biochar amended CLC-Black soil

Biochar†	**N Uptake (kg ha^{-1})**						**P Uptake (kg ha^{-1})**					
	50N+25P‡			**100N+25P**§			**50N+25P**			**100N+25P**		
	Biochar (t ha^{-1})			Biochar (t ha^{-1})			Biochar (t ha^{-1})			Biochar (t ha^{-1})		
	0	1	2	0	1	2	0	1	2	0	1	2
	kg ha^{-1}											
WSB-Fine	41 B **b**¶	43 AB **b**	84 **A a**	45 A ab	64 **A** ab	66 A ab	6 A b	6 AB b	12 A **a**	7 A b	7 A b	8 A ab
FSB-Fine	48 B a	59 **A** a	62 AB a	45 A a	47 AB a	59 A a	6 A a	9 A a	8 A a	5 A a	6 A a	8 A a
WB-Fine	30 C a	32 B a	45 B a	32 A a	34 B a	59 A a	6 A a	4 B a	6 A a	5 A a	6 A a	7 A a
WB-Chunky	66 **A** a	58 AB a	75 AB a	65 A a	46 AB a	68 A a	7 A a	7 AB a	9 A a	7 A a	5 A a	8 A a
ANOVA		**F**	***p***		**SEM**#			**F**	***p***		**SEM**	
WSB-Fine (BRx FT††)		4.31	**0.033**		8.83			3.88	**0.044**		1.30	
FSB-Fine (BR x FT)		1.56	0.242		8.51			3.1	0.075		1.05	
WB-Fine (BR x FT)		0.44	0.651		8.14			0.18	0.836		1.01	
WB-Chunky (BR x FT)		0.24	0.791		7.93			0.25	0.783		1.09	

† WSB-Fine = Wheat straw fine fraction fast pyrolysis biochar; FSB-Fine = Flax straw fine fraction fast pyrolysis biochar; WB-Fine = Willow fine fraction slow pyrolysis biochar; and WB-Chunky = Willow chunky fraction slow pyrolysis biochar

‡ 50 kg N ha^{-1} as urea and 25 kg P_2O_5 ha^{-1} as monoammonium phosphate

§ 100 kg N ha^{-1} as urea and 25 kg P_2O_5 ha^{-1} as monoammonium phosphate

¶ For a given nutrient uptake, means (biochar type, N = 16, R = 4) with the same upper case letter in the same column and means (biochar rates x fertilizer treatment, N = 24, n = 4) with the same lower case letter in the same row are not significantly different (p<0.05). The multi-treatment comparisons were made using the Tukey's HSD method

Standard error of mean

†† Biochar rate (BR) and Fertilizer treatment (FT) interaction

Table 4.7. Nitrogen and phosphorus recovery (%) by canola grown in rotation as first crop in biochar amended CB-Brown soil

Biochar type†	% N Recovery						% P Recovery					
	50N+25P‡			100N+25P§			50N+25P			100N+25P		
	Biochar (t ha^{-1})			Biochar (t ha^{-1})			Biochar (t ha^{-1})			Biochar (t ha^{-1})		
	0	1	2	0	1	2	0	1	2	0	1	2
	%											
WSB-Fine	34 A a¶	47 A a	71 A a	31 A a	38 A a	34 A a	6 A a	7 A a	7 A a	7 A a	7 A a	3 A a
FSB-Fine	27 A a	28 A a	78 A a	28 A a	31 A a	47 A a	8 A a	10 A a	14 A a	8 A a	9 A a	10 A a
WB-Fine	52 A a	62 A a	52 A a	29 A a	48 A a	34 A a	5 A a	6 A a	10 A a	6 A a	16 A a	10 A a
WB-Chunky	44 A ab	47 A a	72 A a	19 A a	53 A a	32 A a	6 A a	6 A a	13 A a	2 A a	17 A a	4 A a
ANOVA		**F**	***p***		**SEM#**			**F**	***p***		**SEM**	
WSB-Fine (BRx FT††)		0.88	0.436		25.37			1.40	0.276		3.38	
FSB-Fine (BR x FT)		0.89	0.433		20.40			0.11	0.897		5.07	
WB-Fine (BR x FT)		0.27	0.763		20.36			4.65	**0.027**		5.64	
WB-Chunky (BR x FT)		3.11	0.074		14.41			2.39	0.120		5.04	

† WSB-Fine = Wheat straw fine fraction fast pyrolysis biochar; FSB-Fine = Flax straw fine fraction fast pyrolysis biochar; WB-Fine = Willow fine fraction slow pyrolysis biochar; and WB-Chunky = Willow chunky fraction slow pyrolysis biochar

‡ 50 kg N ha^{-1} as urea and 25 kg P_2O_5 ha^{-1} as monoammonium phosphate

§ 100 kg N ha^{-1} as urea and 25 kg P_2O_5 ha^{-1} as monoammonium phosphate

¶ For a given nutrient uptake, means (biochar type, N = 16, R = 4) with the same upper case letter in the same column and means (biochar rates x fertilizer treatment, N = 24, n = 4) with the same lower case letter in the same row are not significantly different (p<0.05). The multi-treatment comparisons were made using the Tukey's HSD method

Standard error of mean

†† Biochar rate (BR) and Fertilizer treatment (FT) interaction

Table 4.8. Nitrogen recovery (%) by canola grown in rotation as first crop in biochar amended CLC-Black soil

Biochar type[†]	% N Recovery								
	50N+25P[‡]			100N+25P[§]			BR x FT[¶]		
	Biochar (t ha^{-1})			Biochar (t ha^{-1})			F	*p*	SEM[#]
	0	1	2	0	1	2			
	%								
WSB-Fine	29 A b[††]	31 A b	76 A **a**	23 A b	26 A b	45 A b	5.69	**0.015**	15.70
FSB-Fine	37 A abc	73 A ab	15 A **a**	23 A **bc**	25 A **c**	35 A abc	2.03	0.166	13.92
WB-Fine	29 A a	31 A a	47 A a	24 A a	27 A a	38 A a	0.16	0.854	12.74
WB-Chunky	39 A a	40 A a	53 A **a**	26 A a	31 A a	44 A a	0.51	0.608	18.83

† WSB-Fine = Wheat straw fine fraction fast pyrolysis biochar; FSB-Fine = Flax straw fine fraction fast pyrolysis biochar; WB-Fine = Willow fine fraction slow pyrolysis biochar; and WB-Chunky = Willow chunky fraction slow pyrolysis biochar

‡ 50 kg N ha^{-1} as urea and 25 kg P_2O_5 ha^{-1} as monoammonium phosphate

§ 100 kg N ha^{-1} as urea and 25 kg P_2O_5 ha^{-1} as monoammonium phosphate

¶ Biochar rate (BR) and Fertilizer treatment (FT) interaction

Standard error of mean

†† For a given nutrient uptake, means (biochar type, N=16, R=4) with the same upper case letter in the same column and means (biochar rates x fertilizer treatment, N = 24, n = 4) with the same lower case letter in the same row are not significantly different (p<0.05). The multi-treatment comparisons were made using the Tukey's HSD method

4.5.3 Effects of biochar application on soil nutrient concentrations and chemical properties

4.5.3.1 Effects on soil nutrient concentrations

Soil sampling for analysis of residual nutrient concentration was completed at the end of the first year following canola harvest. Soil samples from different depths were analyzed for available soil NO_3^--N (Table 4.9 and 4.10), and samples from 0-15 cm depth were analyzed for soil available PO_4^+-P concentrations (Table 4.11) at both sites to assess treatment effects on the residual availability of N and P.

Extractable available soil NO_3^--N concentrations were similar among biochar rates for CB-Brown or CLC-Black sites (Table 4.9 and 4.10). The CLC-Black site generally had higher NO_3^--N concentration than the CB-Brown soil, consistent with differences observed at the beginning of the experiment. The content of soil residual available NO_3^--N at both sites did not increase from the application of biochar types. Both the fast pyrolysis biochars (WSB-Fine and FSB-Fine) exhibited a consistent increase in NO_3^--N concentration with increasing biochar rates, but the differences were not significant (p>0.05).

Available soil PO_4^+-P concentrations were found to be similar among biochar rates for CB-Brown or CLC-Black sites (Table 4.11). Both sites generally had similar PO_4^+-P concentration, and no consistent differences were observed after the first year of study (Table 4.11). As well, the content of residual available PO_4^+-P was not affected by biochar types.

Table 4.9. Soil NO_3^--N (kg ha^{-1}) of different depths in biochar amended CB-Brown soil

Soil depth	Biochar type‡	NO_3^--N (kg ha^{-1})†								
		50N+25P§			100N+25P¶			BR x FT#		
		Biochar rate (t ha^{-1})			Biochar rate (t ha^{-1})			F	*p*	SEM††
		0	1	2	0	1	2			
		kg ha^{-1}								
0-15 cm	WSB-Fine	6.5 A a‡‡	7.5 A a	7.2 A a	5.3 A a	6.9 A a	7.08 A a	0.28	0.760	1.14
	FSB-Fine	5.3 A a	6.1 A a	6.6 A a	4.7 A a	17.3 A a	15.9 A a	0.97	0.403	4.93
	WB-Fine	6.1 A a	4.5 A a	6.1 A a	6.5 A a	5.2 A a	9.4 A a	0.78	0.475	1.25
	WB-Chunky	6.4 A a	4.6 A a	6.6 A a	7.6 A a	6.3 A a	4.7 A a	2.32	0.127	0.89
15-30 cm	WSB-Fine	4.1 A a	5.7 A a	5.6 A a	2.5 A a	2.8 A a	2.6 A a	0.48	0.628	0.57
	FSB-Fine	3.1 A a	4.5 A a	4.8 A a	3.3 A a	7.4 A a	4.2 A a	2.61	0.107	2.01
	WB-Fine	4.1 A a	2.5 A a	2.5 A a	2.6 A a	2.5 A a	6.8 A a	1.2	0.327	2.02
	WB-Chunky	3.9 A **a**	2.1 A b	4.4 A ab	2.8 A b	2.2 A b	1.8 A b	3.92	**0.039**	0.76
30-60 cm	WSB-Fine	4.9 A a	6.4 A a	4.9 A a	5.5 A a	6.6 A a	4.4 A a	0.13	0.881	1.21
	FSB-Fine	7.2 A a	6.9 A ab	8.3 A a	5.4 A ab	5.8 A b	5.6 A ab	0.23	0.799	1.22
	WB-Fine	6.9 A a	3.4 A a	7.6 A a	5.2 A a	4.6 A a	6.7 A a	0.31	0.740	1.87
	WB-Chunky	8.3 A a	4.8 A a	5.1 A a	6.7 A a	6.1 A a	4.4 A a	0.46	0.636	1.55

† Soil extractable NO_3^--N (kg ha^{-1})

‡ WSB-Fine = Wheat straw fine fraction fast pyrolysis biochar; FSB-Fine = Flax straw fine fraction fast pyrolysis biochar; WB-Fine = Willow fine fraction slow pyrolysis biochar; and WB-Chunky = Willow chunky fraction slow pyrolysis biochar

§ 50 kg N ha^{-1} as urea and 25 kg P_2O_5 ha^{-1} as monoammonium phosphate

¶ 100 kg N ha^{-1} as urea [$CO(NH_2)_2$] and 25 kg P_2O_5 ha^{-1} as monoammonium phosphate

Biochar rate (BR) and Fertilizer treatment (FT) interaction

†† Standard error of mean

‡‡ For a depth, means (biochar type, N = 16, n = 4) with the same upper case letter in the same column and means (biochar rate x fertilizer treatment, N = 24, n = 4) with the same lower case letter in the same row are not significantly different ($p<0.05$). The multi-treatment comparisons were made using the Tukey's HSD method

Table 4.10. Soil NO_3^--N (kg ha^{-1}) of different depths in biochar amended CLC-Black soil

Soil depth	Biochar type‡	NO_3^--N (kg ha^{-1})†						BR x FT#		
		50N+25P§			100N+25P¶			F	*p*	SEM††
		Biochar rate (t ha^{-1})			Biochar rate (t ha^{-1})					
		0	1	2	0	1	2			
		kg ha^{-1}								
0-15 cm	WSB-Fine	11.9 **A** a‡‡	14.9 A a	15.0 A a†	12.4 A a	12.9 A a	15.6 A a	0.28	0.757	1.77
	FSB-Fine	12.2 **A** a	13.9 A a	13.4 A a	11.8 A a	17.3 A a	13.1 A a	4.94	0.023	1.70
	WB-Fine	11.7 AB a	15.5 A a	10.0 A a	12.1 A a	13.0 A a	15.9 A a	5.63	0.013	1.58
	WB-Chunky	7.4 **B** a	14.1 A a	11.7 A a	11.5 A a	13.2 A a	13.5 A a	1.20	0.325	1.61
15-30 cm	WSB-Fine	7.4 A a	6.8 A a	8.3 A a	7.8 A a	6.2 A a	6.3 A a	1.88	0.182	0.61
	FSB-Fine	6.4 A a	8.1 A a	8.1 A a	8.6 A a	7.1 A a	8.0 A a	1.48	0.258	0.99
	WB-Fine	5.7 A a	6.6 A a	7.0 A a	10.5 A a	5.4 A a	6.1 A a	3.79	**0.042**	1.23
	WB-Chunky	5.4 A b	7.5 A **a**	7.6 A **a**	5.9 A ab	6.4 A ab	6.4 A ab	3.22	0.064	0.39
30-60 cm	WSB-Fine	6.5 A a	9.3 **A** a	10.2 A a	10.7 AB a	7.6 B a	7.1 B a	6.25	**0.009**	1.09
	FSB-Fine	7.5 A c	8.4 AB bc	7.6 A c	16.4 **A a**	14.1 **A a**bc	14.8 **A** ab	0.51	0.610	1.57
	WB-Fine	7.3 A b	7.1 B b	7.0 A b	12.4 AB **a**	8.1 B b	8.1 B b	5.54	**0.013**	0.72
	WB-Chunky	6.8 A a	8.4 AB a	7.4 A a	8.4 **A** a	7.2 B a	6.8 B a	1.94	0.179	0.76

† Soil extractable NO_3^--N (kg ha^{-1})

‡ WSB-Fine = Wheat straw fine fraction fast pyrolysis biochar; FSB-Fine = Flax straw fine fraction fast pyrolysis biochar; WB-Fine = Willow fine fraction slow pyrolysis biochar; and WB-Chunky = Willow chunky fraction slow pyrolysis biochar

§ 50 kg N ha^{-1} as urea and 25 kg P_2O_5 ha^{-1} as monoammonium phosphate

¶ 100 kg N ha^{-1} as urea [$CO(NH_2)_2$] and 25 kg P_2O_5 ha^{-1} as monoammonium phosphate

Biochar rate (BR) and Fertilizer treatment (FT) interaction

†† Standard error of mean

‡‡ For a depth, means (biochar type, N = 16, n = 4) with the same upper case letter in the same column and means (biochar rate x fertilizer treatment, N = 24, n = 4) with the same lower case letter in the same row are not significantly different (p<0.05). The multi-treatment comparisons were made using the Tukey's HSD method

Table 4.11. Soil extractable PO_4^+-P (kg ha^{-1}) of different depths in biochar amended CB-Brown soil at a depth of 0-15 cm

Site	Biochar type‡	PO_4^+-P (kg ha^{-1})†								
		50N+25P§			100N+25P¶			BR x FT#		
		Biochar rate (t ha^{-1})			Biochar rate (t ha^{-1})			F	*p*	SEM††
		0	1	2	0	1	2			
		kg ha^{-1}								
CB-Brown	WSB-Fine	8.2 AB a‡‡	9.8 A a	9.8 A a	11.8 A a	10.8 A a	12.2 A a	0.54	0.591	1.54
	FSB-Fine	12.7 **A** a	11.6 A a	10.0 A a	10.8 A a	10.0 A a	14.0 A a	2.28	0.137	2.22
	WB-Fine	8.2 AB b	9.0 A b	10.0 A b	13.0 A ab	10.4 A ab	17.6 A **a**	1.88	0.187	2.31
	WB-Chunky	7.0 **B** a	9.8 A a	12.6 A a	10.6 A a	10.8 A a	12.6 A a	0.88	0.435	1.54
CLC-Black	WSB-Fine	9.1 B a†	11.1 A a	10.4 A a	10.1 **A** a	9.2 A a	10.5 A a	0.91	0.419	0.83
	FSB-Fine	11.2 AB a	11.1 AB a	11.3 A a	10.0 AB a	9.3 A a	10.0 A a	0.07	0.937	0.97
	WB-Fine	11.6 **A** a	9.2 AB a	10.6 A a	9.0 AB a	9.4 A a	8.7 A a	1.31	0.298	0.88
	WB-Chunky	9.1 B a	9.1 B a	9.8 A a	7.6 B a	9.3 A a	9.3 A a	1.43	0.266	0.56

† Soil extractable PO_4^+-P (kg ha^{-1})

‡ WSB-Fine = Wheat straw fine fraction fast pyrolysis biochar; FSB-Fine = Flax straw fine fraction fast pyrolysis biochar; WB-Fine = Willow fine fraction slow pyrolysis biochar; and WB-Chunky = Willow chunky fraction slow pyrolysis biochar

§ 50 kg N ha^{-1} as urea and 25 kg P_2O_5 ha^{-1} as monoammonium phosphate

¶ 100 kg N ha^{-1} as urea [$CO(NH_2)_2$] and 25 kg P_2O_5 ha^{-1} as monoammonium phosphate

Biochar rate (BR) and Fertilizer treatment (FT) interaction

†† Standard error of mean

‡‡ For a depth, means (biochar type, N = 16, n = 4) with the same upper case letter in the same column and means (biochar rate x fertilizer treatment, N = 24, n = 4) with the same lower case letter in the same row are not significantly different (p<0.05). The multi-treatment comparisons were made using the Tukey's HSD method

4.5.3.2 Effects on soil chemical properties and soil moisture content

A sub-sample from the soil samples that was collected following canola harvest at the end of first year were analyzed for soil pH, EC and % OC (Table 4.12 and 4.13).

The biochar amendment at the two sites had little effect on soil pH. Biochar types showed significant effect and it was observed in the CB-Brown amended with WB-Chunky biochar (2 t ha^{-1}) that this biochar type had significantly (p<0.05) higher pH than the other biochar types. However, it was only 0.3 pH units higher, and of little biological significance. A lack of large liming type effect is explained by low rates of amendment and the highly buffered nature of the two soils. Biochar amendment in the two soils had no effect on soil EC likely due to the low rates of added char. The EC values in all treatments were all much below 1 ds m^{-1} and are considered as non-saline.

Biochar rates did not affect soil % OC content of both sites and is a result of the low application rates of biochar. Gravimetric soil moisture content of different depths following harvests at the end of first year were measured (Appendix B). The biochar amendment at the two sites had little effect on gravimetric soil moisture content. Both biochar rates and biochar types showed no significant effect (p>0.05) on gravimetric soil moisture content or water use efficiency, likely due to the low rates of added char.

Table 4.12. Soil chemical properties (pH, EC, and OC) of 0-15 cm depth in biochar amended CB-Brown soil

Soil properties	Biochar type†	50N+25P‡			100N+25P§			BR x FT¶		
		Biochar rate (t ha^{-1})			Biochar rate (t ha^{-1})			F	*p*	SEM#
		0	1	2	0	1	2			
pH††	WSB-Fine	7.5 A a‡‡	7.2 A a	7.3 AB a	7.1 A a	7.0 A a	7.2 A a	0.51	0.613	0.23
	FSB-Fine	7.3 A a	7.2 A a	7.1 **B** a	7.0 A a	7.1 A a	7.1 A a	0.85	0.446	0.23
	WB-Fine	7.4 A a	7.1 A a	7.1 **B** a	7.3 A a	7.1 A a	7.2 A a	0.27	0.768	0.22
	WB-Chunky	7.4 A a	7.2 A a	7.4 **A** a	7.0 A a	7.2 A a	7.0 A a	1.42	0.272	0.24
		ds m^{-1}								
EC (ds m^{-1}) ††	WSB-Fine	0.30 A a	0.23 A a	0.20 AB a	0.21 A a	0.18 AB a	0.27 A a	1.56	0.242	0.06
	FSB-Fine	0.25 A a	0.20 A a	0.15 **B** a	0.19 A a	0.21 AB a	0.28 A a	2.49	0.117	0.06
	WB-Fine	0.15 A a	0.19 A a	0.15 **B** a	0.21 A a	0.20 B a	0.27 A a	1.46	0.263	0.05
	WB-Chunky	0.26 A a	0.19 A a	0.34 **A** a	0.21 A a	0.24 A a	0.23 A a	0.82	0.458	0.07
		%								
OC (%)	WSB-Fine	1.2 A a	1.4 A a	1.3 A a	1.1 A a	1.2 A a	1.3 A a	1.07	0.369	0.07
	FSB-Fine	1.3 A a	1.4 A ab	1.4 A a	1.2 A ab	1.1 A b	1.4 A ab	1.60	0.230	0.11
	WB-Fine	1.1 A a	1.4 A a	1.4 A a	1.2 A a	1.1 A a	1.4 A a	1.63	0.229	0.10
	WB-Chunky	1.3 A a	1.2 A a	1.2 A a	1.2 A a	1.3 A a	1.2 A a	0.27	0.769	0.13

† WSB-Fine = Wheat straw fine fraction fast pyrolysis biochar; FSB-Fine = Flax straw fine fraction fast pyrolysis biochar; WB-Fine = Willow fine fraction slow pyrolysis biochar; and WB-Chunky = Willow chunky fraction slow pyrolysis biochar

‡ 50 kg N ha^{-1} as urea and 25 kg P_2O_5 ha^{-1} as monoammonium phosphate

§ 100 kg N ha^{-1} as urea and 25 kg P_2O_5 ha^{-1} as monoammonium phosphate

¶ Biochar rate (BR) and Fertilizer treatment (FT) interaction

Standard error of mean

†† pH and Electrical conductivity (EC) of a 1:2 (soil:water) extract

‡‡ For a depth, means (biochar type, N = 16, n = 4) with the same upper case letter in the same column and means (biochar rate x fertilizer treatment, N = 24, n = 4) with the same lower case letter in the same row are not significantly different (p<0.05). The multi-treatment comparisons were made using the Tukey's HSD method

Table 4.13. Soil chemical properties (pH, EC, and OC) of 0-15 cm depth in biochar amended CLC-Black soil

Soil properties	Biochar type†	50N+25P‡			100N+25P§			BR x FT¶		
		Biochar rate (t ha^{-1})			Biochar rate (t ha^{-1})			F	*p*	SEM#
		0	1	2	0	1	2			
pH††	WSB-Fine	7.9 **A** ab‡‡	7.6 A b	7.8 **A** ab	8.0 **A a**	7.8 A ab	7.8 A ab	0.53	0.597	0.08
	FSB-Fine	7.5 AB ab	7.5 A ab	7.2 B b	7.7 B ab	8.0 A **a**	7.9 A ab	0.77	0.480	0.15
	WB-Fine	7.1 B b	7.4 A ab	7.1 B ab	7.9 AB **a**	7.9 A **a**	7.8 A ab	0.50	0.618	0.17
	WB-Chunky	7.4 AB b	7.7 A ab	7.9 **A a**	7.7 B ab	8.0 A **a**	7.9 A **a**	1.02	0.381	0.09
		ds m^{-1}								
EC (ds m^{-1})††	WSB-Fine	0.51 A ab	0.36 A b	0.53 **A** ab	0.52 AB ab	0.41 A ab	0.59 A **a**	0.18	0.834	0.05
	FSB-Fine	0.45 A a	0.36 A a	0.31 AB a	0.54 **A** a	0.50 A a	0.60 A a	1.26	0.308	0.07
	WB-Fine	0.28 A bc	0.36 A bc	0.22 B **c**	0.54 **A** ab	0.50 A abc	0.68 A **a**	2.99	0.081	0.07
	WB-Chunky	0.40 A a	0.44 A a	0.51 **A** a	0.35 B a	0.50 A a	0.56 A a	0.42	0.666	0.07
		%								
OC (%)	WSB-Fine	2.9 A ab	2.6 A b	3.0 A ab	2.9 AB ab	2.6 B b	3.3 A **a**	0.56	0.582	0.16
	FSB-Fine	3.4 A **a**	2.6 A b	3.3 A ab	3.4 **A** ab	3.0 B ab	3.3 A ab	0.85	0.446	0.18
	WB-Fine	2.7 A a	2.9 A a	2.9 A a	3.3 **A** a	3.7 **A** a	3.2 A a	0.41	0.671	0.31
	WB-Chunky	2.6 A a	2.5 A a	3.0 A a	2.5 B a	3.0 B a	3.1 A a	2.58	0.104	0.15

† WSB-Fine = Wheat straw fine fraction fast pyrolysis biochar; FSB-Fine = Flax straw fine fraction fast pyrolysis biochar; WB-Fine = Willow fine fraction slow pyrolysis biochar; and WB-Chunky = Willow chunky fraction slow pyrolysis biochar

‡ 50 kg N ha^{-1} as urea and 25 kg P_2O_5 ha^{-1} as monoammonium phosphate

§ 100 kg N ha^{-1} as urea and 25 kg P_2O_5 ha^{-1} as monoammonium phosphate

¶ Biochar rate (BR) and Fertilizer treatment (FT) interaction

Standard error of mean

†† pH and Electrical conductivity (EC) of a 1:2 (soil:water) extract

‡‡ For a depth, means (biochar type, N = 16, n = 4) with the same upper case letter in the same column and means (biochar rate x fertilizer treatment, N = 24, n = 4) with the same lower case letter in the same row are not significantly different (p<0.05). The multi-treatment comparisons were made using the Tukey's HSD method

4.6 Discussion

4.6.1 Effects of biochar application on crop biomass and grain yield

The results observed in the field study indicate that different sources of biochar performed differently in affecting yield, but only at the CLC-Black site, with no significant effects (p>0.05) observed at the CB-Brown site. Similar to the controlled environment pot studies (Chapter 3), indication of yield enhancement was found for the fast pyrolysis wheat and flax straw fine biochar amendments at the CLC-Black site. Biochar application to soils is reported to increase yield of crops (Lehmann and Joseph, 2009; Woolf et al., 2010; Spokas et al., 2012; Kloss et al., 2013) in controlled environments as well as in the field (Lehmann and Rondon 2006; Chan et al., 2007; Asai et al., 2009; Chan and Xu, 2009). In agreement with the findings of these researchers and other, the effect does appear to be dependent on the soil and biochar type.

Among the two field sites, the CLC-Black Chernozem soil, characterised by higher organic matter content, along with higher soil available N content appeared to be more responsive in yield to biochar amendment than CB-Brown Chernozem soils. This yield increase upon biochar addition in CLC-Black soil may be attributed to the higher SOM content. This higher OM content may result in greater ability to compensate for any N immobilization induced by biochar. Also, slight increase in OC and pH in CLC-Black soil from the biochar may have been beneficial to increase the availability of soil nutrients to plants. The excessive moisture received in the spring of 2012 at the CLC-Black site would also be conducive to N losses by leaching and denitrification, and the WSB-Fine biochar may have helped to reduce loss. Due to slight increase in OC and pH, mineralisation of native soil N may have been increased due to the addition of biochar (Hamer et al., 2004). This increased native soil N may be a result of the priming effect. Hamer et al. (2004) demonstrated that biochar (from maize and rye residues) in soils can promote mineralisation of labile C compounds as a result of enhanced growth of microorganisms. Further research is needed to test this hypothesis. The increased yield may be associated with less denitrification loss of N after treatment addition. Kammann et al. (2012) added peanut (*Arachis hypogaea* L.) hull biochar at 50 Mg ha^{-1} to a German Luvisol and then grew ryegrass (*Lolium perenne* L.). The authors observed a significant increase in biomass yield when compared to controls. The cause of the increase in yield was unknown, but it was

speculated to be a function of reduced N loss to denitrification and hence greater N uptake by plants grown in the presence of biochar.

In the second year, growing wheat, no residual response to biochar types for crop yield was observed in the CB-Brown soil, possibly due to removal of available nutrients by canola grown as the first crop in rotation, with subsequently reduced nutrient availability for wheat. The wheat grown in CLC-Black soil showed considerable variations in yield increment from increasing rate of biochar in some cases. Among the biochar types, the wheat straw fast pyrolysis biochar did produce a yield increase. This may be due to the higher retention of residual nutrients by the WSB-Fine biochar product that could be taken up by the wheat in the following year. Compared to other forms of soil amendments, biochar is reported to have a higher sorption affinity for a range of organic and inorganic compounds, and higher nutrient retention ability (Bucheli and Gustafsson, 2000; Allen-King et al., 2002; Bucheli and Gustafsson, 2003; Nguyen et al., 2008). It has been noted that biochar at high application rates (10 or 20 %, $^{w}/_{w}$) can effectively increase sorption capacities and effectively reduce NH_4^+-N leaching (Lehmann et al., 2003), depending on biochar type and soil and their aging. Singh et al. (2010) added wood and poultry litter based biochars produced at 550 °C to an Alfisol, and observed that freshly added biochars had little effect on initial NH_4^+-N leaching, but upon aging in soil (around 5 months), reduced leaching of NH_4^+-N by 55-65 %. In contrast, however, no sorption effects have been observed with the biochars produced from the same feedstocks at 400 °C.

In this study, both fast pyrolysis biochars (wheat straw and flax straw produced fine fraction biochar) performed better in terms of yield increase than slow pyrolysis biochar. Brewer et. al. (2009) reported that slow and fast pyrolysis process produced biochars with different physicochemical qualities that provide differential effects in the soil environment upon application. For example, biochars produced under high-temperature pyrolysis (>550 °C), are highly aromatic and recalcitrant in nature (Singh and Cowie, 2008), generally have high surface areas (Downie et al., 2009; Keiluweit et al., 2010), and increased CEC that act as a good adsorbents (Mizuta et al., 2004; Lima and Marshall, 2005).

In the present study, there were no biochar and fertilizer interactions and contribution to yield increment. Occasionally, larger yield increases have been reported with biochar additions applied together with inorganic or organic fertilizer treatments (Glaser et al., 2002; Chan et al.,

2007; Steiner et al., 2007; Van Zwieten et al., 2007; Asai et al., 2009; Blackwell et al., 2009). A combination of ability to raise soil pH (Hoshi, 2001; Yamato et al., 2006; Rondon et al., 2007; Van Zwieten et al., 2007;), improve physical properties such as water holding capacity (Iswaran et al., 1980; Chan and Xu, 2009) and retain soil nutrients and reduce leaching losses (Hoshi 2001; Lehmann et al., 2003; Lehmann, 2007a) likely contributes to its ability to increase plant productivity. It is evident that some biochars are effective at retaining nutrients due to high adsorptive capacity. But most of the aforementioned studies used very high rates of biochar treatment in their experiment. For example, Chan et al. (2007) in their study with green-waste biochar impact on radish, observed that the application of greenwaste biochar alone to a hardsetting soil did not result in significant increases in radish dry matter yield, even at the highest rate of application (100 t ha^{-1}). However, significant yield increases were observed when biochar was applied together with the fertilizer, highlighting the role of biochar in improving N fertilizer use efficiency. In contrast, in the present study, the low rate of biochar used may not have been to create some significant nutrient retention in the field sites.

4.6.2 Effects of biochar application on fertilizer uptake and recovery

Biochar addition to the CB-Brown soil did not significantly (p>0.05) affect canola N and P uptake and recovery for all biochar types. However, canola grown in biochar amended soils sporadically showed higher mean N uptake and % recovery compared to the unamended controls, and was significant for wheat straw fine fraction biochar type added to the CLC-Black soil. The increased nutrient uptake in CLC-Black soils associated with the wheat straw biochar was associated with an increase in biomass nutrient concentrations (Table 4.10). Since wheat was grown in rotation as the second crop, higher uptake by canola would deplete the available nutrient for the subsequent wheat crop (data not shown).

Usually, soil amended with biochar is found to have higher nutrient retention than unamended soils (Ding et al., 2010). In this study, the biochar effect seems most pronounced in the CLC-Black soil. Steiner et al. (2008) applied 11 t ha^{-1} wood charcoal to an Oxisol and grew sorghum. They found significantly greater retention of N in soil in the charcoal amended plots in comparison to only mineral fertilized plots. Wardle et al. (1998) found greater tree seedling growth, N uptake, and enhanced efficiency of nutrient uptake in boreal forest soils when charcoal

was added. Both authors indicated that nutrients other than N were more important to enhance plant growth leading to N sequestration in biomass (Steiner et al., 2007).

The increased uptake of applied N by plants on plots with biochar may be explained by either reduced N leaching (Lehmann et al., 2003) or reduced gasesous N losses (Yanai et al., 2007). Reduced N leaching may be a result of either improved retention of the applied N by electrostatic adsorption to exchange sites provided by the biochar or of N immobilization by microbial biomass. Lehmann et al. (2003) suggested microbial immobilization is responsible for decreases in foliar N contents and total N uptake as a response to charcoal additions due to their higher C: N ratio. However, their pot experiment used larger amounts of applied charcoal (67.6 and 135.2 t ha^{-1}) than our study. An assessment of N losses from leaching and denitrification as affected by biochar addition would be recommended for future research in prairie soils.

As in the growth chamber studies (Chapter 3), a few instances of enhanced fertilizer P recovery by canola with biochar addition were observed in this study at both sites. The mechanism for this is not known, but could be related to reduced P fixation on the solid phase, enhanced root growth and beneficial conditions in the rhizosphere.

4.6.3 Effects of biochar application on residual soil nutrient concentrations, chemical properties and soil moisture contents

4.6.3.1 Effects on soil nutrient concentrations

Biochar affects nutrient cycling, potentially affecting nutrient retention and availability when applied to soils. In this study, soil extractable NO_3^--N, and PO_4^+-P concentrations remaining in both soils after canola harvest were found to be largely unaffected by biochar addition. Both the fast pyrolysis biochars (wheat straw fine fraction and flax straw fine fraction) exhibited a consistent increase in NO_3^--N concentration with increasing biochar rates, though the rates of increase were not significant (p>0.05).

Soil extractable NO_3^--N, and PO_4^+-P concentrations were found to be largely unaffected likely due to the low rates of added char. Biochar produced under high-temperature pyrolysis (>550 °C), are highly aromatic and recalcitrant in nature (Singh and Cowie, 2008), generally have high surface areas (Downie et al., 2009; Keiluweit et al., 2010), and CEC that have been

reported to act as a good adsorbents (Mizuta et al., 2004; Lima and Marshall, 2005). Major et al. (2012) studied nutrient leaching in a Columbian Oxisol following a 20 t ha^{-1} high pyrolysis (500 to 700 °C) biochar application and found nutrient leaching with biochar applications relative to unamended soils was greater to the 0.6 m depth than to the 1.2 m depth. The authors suggest that biochar may have influenced nutrient retention throughout the root zone. In contrast, in a California Alfisol, Sarkhot et al. (2012) added the equivalent of 20 t ha^{-1} slow pyrolysis biochar (300 °C) as is or enriched in nutrients from dairy manure effluent. Nitrogen leaching losses with both biochars were similar to unamended soil. Compared with biochars produced at high temperatures, application of biochars produced at low pyrolysis temperatures have shown less Ca, Mg, and NO_3^--N leaching in the literature, likely due to immobilization, because biochars produced at 250 °C contain substantial amounts of bioavailable C similar to the hydrochar reported by Gajić and Koch (2012). Slow and fast pyrolysis results in biochars with different physicochemical qualities thus providing differential effects in the soil environment upon application (Brewer et al., 2009).

4.6.3.2 Effects on soil chemical properties

Biochars, due to their content of bases, typically act as a liming agent, resulting in increased pH when added to soil. Especially in an acid soil, this increased pH can subsequently stimulate microbial activity, thereby further promoting mineralization or decomposition of existing SOM and increasing nutrient availability for a number of soil types (Glaser et al. 2002; Lehmann and Rondon, 2006; Van Zweiten et al., 2007). In this study, biochar types did not produce significant measurable increases in soil pH. Mbagwu and Piccolo (1997) reported that biochar can increase the pH of various soils and textures by up to 1.2 pH units. Several reports have confirmed the liming type effect of biochar on acidic Ultisols (Yuan and Xu, 2011; Yuan et al., 2011) and the improvement of crop growth from biochar amendment of a typical Ultisol may result from an increase of pH and CEC (Peng et al., 2011).However this biochar induced increase in pH is mostly is process- and rate-dependent (Hass et al., 2012). The low biochar rate used in these studies explains why there was no impact on soil pH. The pH of both soils did not change much upon biochar addition, possibly because of the low biochar rates used and that both soils were already highly buffered by relatively high clay and organic C content compared to some tropical soils (McCauley et al., 2009; McElligott et al., 2011). In an 8-week incubation study,

Hass et al. (2012) evaluated slow-pyrolysis chicken manure biochars (produced at 350 and 700 °C), amended at 5, 10, 20, and 40 g kg^{-1} with or without dolomitic lime (AgLime) into a highly weathered acid Gilpin soil (fine-loamy, mixed, active, mesic Typic Hapludult). Soil amended with high rate of biochar (40 g kg^{-1}) produced from higher temperatures (700 °C) increased soil pH from 4.8 to 6.6 at the high application rate but was less effective than AgLime.

Biochar amendment in both soils had little effect on soil EC and OC; likely due to the low rates of added char. Biochars are suggested to have long residence times in many ecosystems (Mann, 2008). A trend towards increased SOC concentrations does point towards a C sequestration effect in these two soils, one that may only be possible to detect at rates of biochar amendment higher than what was used in the current study.

4.6.3.3 Effects on soil moisture contents

Biochar has a higher surface area and greater porosity relative to other types of SOM, and can therefore improve soil structure and aggregation, which can improve water retention in soil (Piccolo and Mbagwu 1990; Piccolo et al. 1996; Mbagwu and Piccolo 1997). These physical properties in biochar occur at a range of scales and affect the proportion of water than can be retained. In our studies, biochar did not affect soil moisture content measured at both sites. The CB-Brown soil is sandy loam in texture with very low organic matter content and CLC-Black was clay-loam with relatively greater OM content. A loamy textural characteristic along with low rate of biochar application explains the lack of effect on soil moisture content or water use efficiency. Glaser et al. (2002) reported that Anthrosols enriched with charcoal had surface areas three times higher than those of surrounding Oxisols, and had an increased field capacity of 18 %. However, their rates of application were much higher than in the present study. Tryon (1948) studied the effect of charcoal on the percentage of available moisture in soils of different textures and found different responses among soils. In sandy soil, the addition of charcoal increased available moisture after adding 45 % biochar by volume, while no changes were observed in loamy soil, and soil available moisture decreased in the clayey soil. The high surface area of biochar can lead to increased water retention, although the effect seems to depend on the initial texture of the soil. Improved water holding capacity with biochar additions is most commonly observed in coarse-textured or sandy soils and seems to require application rates of several hundred t ha^{-1} (Glaser et al. 2002; Gaskin et al. 2007). The impact of biochar additions on

moisture content may be due to increased surface area relative to that found in coarse-textured soils (Glaser et al. 2002). Therefore, improvements in soil water retention by biochar additions may only be expected in very coarse-textured soils or soils with large macropore volume. Additionally, a large amount of biochar may need to be applied to the soil before it increases water retention.

4.7 Conclusion

The addition of four different biochars at two application rates in combination with different N and P fertilizer rates to two Saskatchewan field sites showed that the effect of biochar application on crop yield, nutrient uptake and recovery, and soil chemical properties is dependent on soil and biochar types. Biochar addition increase canola and wheat biomass yield only on one soil: the Black Chernozem, and only for one biochar type: a wheat straw fast pyrolysis fine biochar. In agreement with the pot study results (Chapter 3), fast pyrolysis fine biochars with high CEC appeared to be more effective in promoting crop growth and nutrient uptake and recovery. Wheat grown as the second crop in the rotation showed little response to biochar amendment, likely as a result of nutrient depletion by the previous canola crop. In both soils, biochars at the rates applied (1 and 2 t ha^{-1}) had no significant effect (p>0.05) on EC, OC concentrations, or soil moisture content.

5. Overall Synthesis and Conclusions

5.1 Summary of findings

Biochar application to soil potentially has beneficial impacts on soil properties and plant growth. Investigation of the effects of biochar on crop growth has mainly concentrated on nutrient poor soils in sub-tropical and tropical regions, and little is known about its effects on soils of the northern Great Plains such as those in Saskatchewan. Understanding the characteristics of different biochars and evaluation of the effects of biochar on soils and crop yield in prairie soils is needed to better assess the utility of biochar as a soil amendment in Saskatchewan. This MSc thesis research examined the response of canola and wheat grown in rotation to the application of different biochar sources at two different rates, alone and in combination with commercial inorganic N and P fertilizers, under both controlled environment and field conditions. Evaluation under controlled conditions (Chapter 3) provided valuable data to accompany the field study (Chapter 4) that were conducted with similar treatments.

The results of the growth chamber studies (Chapter 3) with five different biochars added at two rates to two contrasting Saskatchewan soils under controlled environment conditions showed that the effect of biochar application on crop yield, nutrient recovery and soil properties is dependent on soil type and was found to differ among the biochar types. Biochar addition tended to increase canola biomass yield and nutrient recovery on the Black Chernozem, a soil with higher organic matter but lower pH than the Brown Chernozem, where fewer significant effects were observed. Fast pyrolysis fine biochars with high CEC appeared more effective in promoting canola growth and nutrient uptake than chunky ones produced under slow pyrolysis. Wheat grown after the canola showed little response to biochar amendment, likely as a result of nutrient depletion by the preceding canola crop. In both soils, biochar did not greatly alter residual soil extractable nutrient content, and had no significant effect ($p>0.05$) on pH, EC or OC concentrations.

The effects of the biochar amendments under actual field conditions were evaluated (Chapter 4). The addition of four different biochars at two application rates in combination with different N and P fertilizer rates at two Saskatchewan field sites near Central Butte and Prince Albert also showed that the effect of biochar application on crop yield, nutrient uptake and recovery and soil chemical properties is dependent on soil and biochar types, as found in growth chamber studies. In the 2012 and 2013 growing seasons in which the studies were conducted, conditions were colder and wetter than normal, especially for the Black Chernozem at Prince Albert. Biochar addition increased canola and wheat biomass yield only on one soil: the Black Chernozem, and only for one biochar type: a wheat straw fast pyrolysis fine biochar. In agreement with the pot study results (Chapter 3), fast pyrolysis fine biochars with high CEC appeared to be more effective in promoting crop growth and nutrient uptake and recovery. Wheat grown as the second crop in the rotation showed little response to biochar amendment, likely as a result of nutrient depletion by the previous canola crop. In both soils, biochars at the rates applied (1 and 2 t ha^{-1}) had no significant effect on EC, OC concentrations, or soil moisture content.

Of the tested five biochars, two fast pyrolysis biochars were observed to be effective in the growth chamber study, whereas only wheat straw fast pyrolysis fine biochar was found to be effective in the field site experiments. Both fast pyrolysis biochars were found to have a significant effect on biomass yield, and recovery of applied N and P fertilizers for two soils under identical environmental conditions in the growth chamber, while only one soil: CLC-Black showed any response in the field. The level of environmental variation (site and year) encountered in the field has the potential to influence crop and soil response to biochar amendment.

5.2 Implications and recommendations

5.2.1 Choice of biochar

Biochar produced from different feedstock is known to play an important function in nutrient cycling. Five different biochars were tested in growth chamber (Chapter 3) and four biochars of the biochars were used in the field study (Chapter 4). These biochars were produced from different locally available biomass sources under fast and slow pyrolysis conditions. The

two fast pyrolysis fine fraction biochars (wheat straw fine fraction and flax straw fine fraction) appeared more effective in promoting canola growth and nutrient uptake, especially in the Black Chernozem soil. Overall, in this study the fast pyrolysis fine biochars with high CEC appeared to be more effective in promoting crop growth and nutrient uptake and recovery. Therefore, it can be recommended that locally available crop residues like wheat and flax straw can be used to produce biochars to be added as soil amendments to improve soil conditions for crop growth.

5.2.2 Rate of biochar

Most previous studies have been conducted with very high (tens to hundreds of t ha^{-1}) rates of biochar application, but such rates may be considered impractical for application of dry chars, due to the very low density and powdery nature that makes them difficult to transport and apply safely and uniformly, especially in the windy southern Canadian prairies. In this study, relatively low rates of biochar (1 and 2 t ha^{-1}) were utilized in both growth chamber and field studies. Based on the results of this research, biochar applications at rates of 1-2 t ha^{-1} to Prairie Chernozem soils will not have large effects on soil properties or plant growth

5.2.3 Impact on soil properties

The origin of the concept that biochar can be beneficial to soil fertility comes from studies of the Amazonian Dark Earth soils known as Terra Preta and Terra Mulata which contain high levels of BC (Glaser, 2001). Different biochars applied at two application rates (1 and 2 t ha^{-1}) to two contrasting Saskatchewan soils did not have large impact on soil nutrient contents and had no measurable effects on pH, EC, OC or soil moisture. Therefore, it can be suggested that all of the biochars tested would be safe to apply at low rates (1-2 t ha^{-1}) in Saskatchewan Chernozem soils.

5.3 Future research

The fundamental mechanisms by which biochar could provide benefits to the prairie Chernozem soils and the wider functioning of the agro-ecosystem are still poorly understood. Some unknowns should be addressed before large-scale use of biochar for agricultural purposes in Saskatchewan soils could be recommended. Hamer et al. (2004) demonstrated that biochar amendment in soils can promote mineralization of labile-C compounds as a result of enhanced

growth of microorganisms. Further research is needed on the impact of biochar amendment on specific microbial transformations in soil such as mineralization, nitrification, and denitrification.

Evaluation under a wider range of crop, soil and environmental conditions and the interaction with biochar feedstock, production method, and application rate should be investigated before large scale deployment of biochar as a soil amendment can be contemplated in Saskatchewan. Nonetheless, there is evidence in the studies that at least for some soil/crop and biochar type combinations, addition of biochar may be beneficial.

In growth chamber and field studies, occasional depressions in crop biomass yield were observed in both crops for both soils (Chapter 3 and 4). The results of our studies suggest that despite additional mineral fertilization, short-term growth inhibition could occur when applying biochar to temperate prairie soils. In these calcareous Chernozems, biochar amendment did not greatly alter the availability of N and P, and its effects on soil pH, OC, and EC were minor and often non-significant. Therefore, some efforts are warranted to explore the root causes of any yield depressions associated with biochar amendments. Specialized equipment or alteration of the physical form of the biochar may be required for successful biochar utilization, as the powdery biochar utilized in this thesis research was difficult to handle and apply. More effort is required to develop methods for processing biochar materials to make them easier to employ.

Finally, it is imperative to understand the impact of long term (i.e., several years) application of biochar on crop yield and soil quality of prairie soils. Although biochar as a soil amendment for improving soil quality and soil C sequestration has attracted much attention, there is inadequate knowledge on the effects of repeated applications of biochars made over several years.

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7. APPENDICES

7.1 Appendix A: Effects of biochar in combination with low fertilizer rates on yield, and soil properties in a canola-wheat rotation grown under controlled environmental conditions

Table A.1. The influence of biochar, fertilizer and their interaction on crop biomass yield

Sources of variation	CB-Brown				CLC Black			
	Canola		Wheat		Canola		Wheat	
	F	*P*†	F	*P*	F	P	F	*P*
WSB-Fine								
Biochar rate	7.62	0.001	4.70	0.013	3.61	0.034	12.26	0.001
Fertlizer Treatment	153.20	0.001	13.26	0.001	46.56	0.001	8.86	0.001
BR x FT‡	2.21	0.031	0.89	0.552	3.01	0.005	0.84	0.589
FSB-Fine								
Biochar rate	2.35	0.106	0.74	0.483	26.57	0.001	0.07	0.933
Fertlizer Treatment	22.55	0.001	14.01	0.001	20.83	0.001	1.97	0.098
BR x FT	0.47	0.902	1.54	0.150	1.95	0.058	3.82	0.001
WB-Fine								
Biochar rate	5.01	0.010	2.23	0.108	5.27	0.008	1.72	0.188
Fertlizer Treatment	101.03	0.001	7.26	0.001	38.64	0.001	2.68	0.031
BR x FT	3.04	0.004	1.41	0.202	1.73	0.098	2.14	0.037
WB-Chunky								
Biochar rate	2.47	0.094	0.78	0.465	2.71	0.076	4.35	0.018
Fertlizer Treatment	145.26	0.001	3.70	0.006	39.75	0.001	4.06	0.003
BR x FT	0.46	0.905	0.83	0.605	1.19	0.318	0.63	0.782
WSB-Chunky								
Biochar rate	1.42	0.251	11.41	0.001	0.08	0.923	5.00	0.010
Fertlizer Treatment	91.56	0.001	16.29	0.001	45.46	0.001	6.46	0.001
BR x FT	2.07	0.044	3.43	0.002	1.16	0.339	2.34	0.023

† P values for treatment effects and interaction terms and comparisons derived from an ANOVA ($p<0.05$)

‡ Biochar rate and Fertilizer treatment interactions

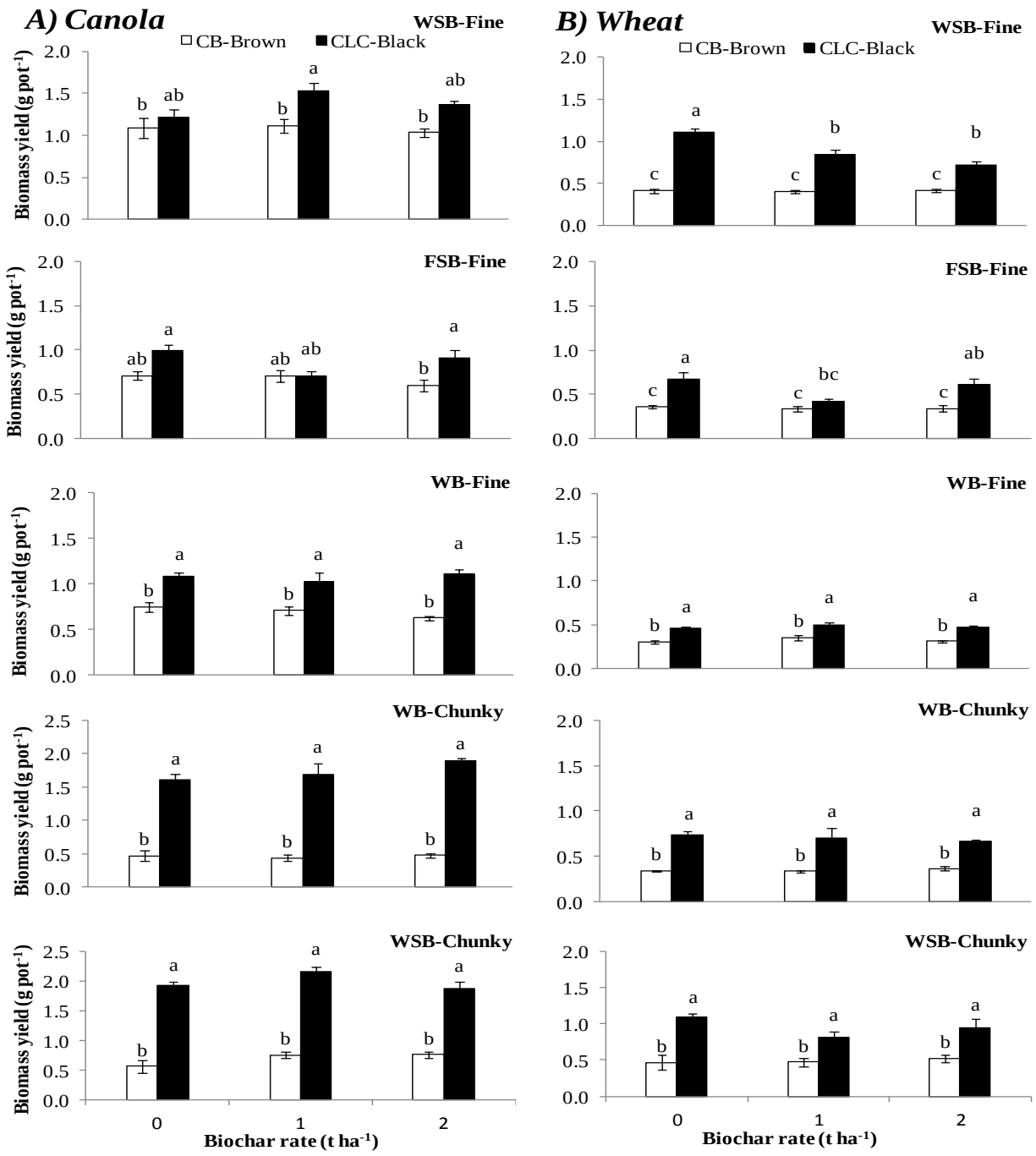

Fig. A.1. Mean biomass yield (g pot^{-1}) of canola followed by wheat in rotation in biochar amended CB-Brown and CLC-Black soil in a growth chamber experiment. All treatments received 50 kg N ha^{-1} and 25 kg P_2O_5 ha^{-1} fertilizer. Error bars are standard error of mean (soil x biochar rate) with N = 24 and n = 4. (WSB-Fine = Wheat straw fine fraction fast pyrolysis biochar; FSB-Fine = Flax straw fine fraction fast pyrolysis biochar; WB-Fine = Willow fine fraction slow pyrolysis biochar; WB-Chunky = Willow chunky fraction slow pyrolysis biochar; and FSB-Chunky = Wheat straw chunky fraction slow pyrolysis biochar). For a crop and biochar type, means with different letters are significantly different (Tukey's HSD, p<0.05)

Table A.2. Biochar amendment effects on nitrogen uptake (mg pot^{-1}) by canola and wheat grown in rotation in CB-Brown and CLC-Black soil

Biochar type†	CANOLA							WHEAT					
	CB-Brown Soil‡			CLC-Black soil‡				CB-Brown Soil			CLC-Black soil		
	Biochar (t ha^{-1})			Biochar (t ha^{-1})				Biochar (t ha^{-1})			Biochar (t ha^{-1})		
	0	1	2	0	1	2		0	1	2	0	1	2
	.....			.....			mg	.....			.....		
WSB-Fine	9.0 b§	8.9 b	8.5 b	15.7 a	15.6 a	14.6 a		3.5 c	3.5 c	2.7 c	9.2 **a**	7.9 **a**	5.6 a
FSB-Fine	8.1 bc	8.4 bc	6.6 c	10.7 ab	5.9 c	12.4 **a**		2.7 b	2.4 b	2.0 b	6.1 a	5.8 a	5.9 a
WB-Fine	8.8 bc	7.2 c	6.2 c	13.1 a	13.2 a	11.4 ab		2.3 b	2.5 b	1.7 b	5.9 a	6.6 a	6.1 a
WB-Chunky	3.3 b	3.0 b	3.5 b	22.8 a	20.2 a	21.0 a		3.1 b	3.1 b	3.0 b	6.0 a	6.4 a	5.9 a
WSB-Chunky	4.2 b	4.4 b	6.8 b	21.8 a	23.4 a	24.0 a		3.5 b	2.7 b	3.7 b	6.8 a	6.9 a	5.8 a
ANOVA		**F**	***p***		**SEM#**				**F**	***p***		**SEM#**	
WSB-Fine													
Soil x Biochar rate		0.13	0.877		0.660				12.34	**0.004**		0.295	
FSB-Fine													
Soil x Biochar rate		17.13	**0.001**		0.718				0.16	0.849		0.525	
WB-Fine													
Soil x Biochar rate		0.74	0.489		0.694				0.76	0.483		0.306	
WB-Chunky													
Soil x Biochar rate		0.83	0.454		0.928				0.43	0.659		0.308	
WSB-Chunky													
Soil x Biochar rate		0.25	0.784		1.307				4.32	**0.029**		0.372	

† WSB-Fine = Wheat straw fine fraction fast pyrolysis biochar; FSB-Fine = Flax straw fine fraction fast pyrolysis biochar; WB-Fine = Willow fine fraction slow pyrolysis biochar; WB-Chunky = Willow chunky fraction slow pyrolysis biochar; and FSB-Chunky = Wheat straw chunky fraction slow pyrolysis biochar

‡ All treatments received 50 kg N ha^{-1} as urea and 25 kg P_2O_5 ha^{-1} as monoammonium phosphate

§ For a crop, means (soil x biochar rate) with the same letter in the same row are not significantly different (p<0.05) (N = 24, n = 4). The multi-treatment comparisons were made using the Tukey's HSD method

Standard error of mean

Table A.3. Biochar amendment effects on phosphorus uptake (mg pot^{-1}) by canola and wheat grown in rotation in CB-Brown and CLC-Black soil

Biochar type†	CANOLA							WHEAT						
	CB-Brown Soil‡			CLC-Black soil‡				CB-Brown Soil			CLC-Black soil			
	Biochar (t ha^{-1})			Biochar (t ha^{-1})				Biochar (t ha^{-1})			Biochar (t ha^{-1})			
	0	1	2	0	1	2		0	1	2	0	1	2	
	mg													
WSB-Fine¶	3.3 a§	3.2 a	3.2 a	1.9 b	2.4 b	2.3 b		0.5 b	0.6 b	0.5 b	1.0 a	1.1 a	1.1 a	
FSB-Fine	1.8 ab	2.0 a	1.6 ab	1.7 ab	1.4 b	1.8 ab		0.4 a	0.4 a	0.4 a	0.6 a	0.5 a	0.6 a	
WB-Fine	1.8 a	1.7 a	1.6 a	1.7 a	1.7 a	1.6 a		0.4 a	0.4 a	0.4 a	0.5 a	0.5 a	0.5 a	
WB-Chunky	1.6 bc	1.0 c	1.9 ab	2.4 a	2.3 ab	2.6 a		0.9 a	1.1 a	1.0 a	0.6 b	0.4 b	0.5 b	
WSB-Chunky	2.0 a	2.6 a	2.6 a	3.1 a	3.0 a	2.7 a		1.2 a	1.2 a	1.1 a	1.6 a	1.2 a	1.3 a	
ANOVA		**F**	***p***		**SEM#**				**F**	***p***		**SEM#**		
WSB-Fine														
Soil x Biochar rate		1.48	0.253		0.142				1.480	0.254		0.103		
FSB-Fine														
Soil x Biochar rate		6.92	**0.006**		0.103				0.19	0.828		0.086		
WB-Fine														
Soil x Biochar rate		0.46	0.640		0.102				0.12	0.891		0.048		
WB-Chunky														
Soil x Biochar rate		1.89	0.180		0.017				7.38	**0.005**		0.057		
WSB-Chunky														
Soil x Biochar rate		1.96	0.170		0.243				1.08	0.359		0.130		

† WSB-Fine = Wheat straw fine fraction fast pyrolysis biochar; FSB-Fine = Flax straw fine fraction fast pyrolysis biochar; WB-Fine = Willow fine fraction slow pyrolysis biochar; WB-Chunky = Willow chunky fraction slow pyrolysis biochar; and FSB-Chunky = Wheat straw chunky fraction slow pyrolysis biochar

‡ All treatments received 50 kg N ha^{-1} as urea and 25 kg P_2O_5 ha^{-1} as monoammonium phosphate

§ For a crop, means (soil x biochar rate) with the same letter in the same row are not significantly different (p<0.05) (N = 24, n = 4). The multi-treatment comparisons were made using the Tukey's HSD method

Standard error of mean

Table A.4. Biochar amendment effects on recovery of applied nitrogen fertilizer by canola and wheat grown in rotation in CB-Brown and CLC-Black soil

Biochar type†	CANOLA							WHEAT					
	CB-Brown Soil‡			CLC-Black soil‡				CB-Brown Soil			CLC-Black soil		
	Biochar (t ha^{-1})			Biochar (t ha^{-1})				Biochar (t ha^{-1})			Biochar (t ha^{-1})		
	0	1	2	0	1	2		0	1	2	0	1	2
	.....			.....			%	.....			.....		
WSB-Fine	22.5 bc§	21.9 bc	21.2 bc	32.9 ab	43 a	14.6 c		-1.3 b	-1.5 b	-4.1 b	10 **a**	0.3 b	-1.3 b
FSB-Fine	18.8 a	21.8 a	14.2 ab	20.0 a	7.0 ab	13.5 ab		2.9 a	2.3 a	-0.3 a	-1.6 a	1.0 a	0.8 a
WB-Fine	19.2 ab	16.3 b	15.1 b	23.7 ab	31.3 ab	12.6 b		-1.0 ab	-0.3 ab	-3.0 ab	4.2 a	5.2 a	-0.6 ab
WB-Chunky	6.6 b	7.3 b	8.2 b	40.0 a	41.3 a	44.5 a		1.7 a	2.7 a	2.1 a	1.3 a	1.1 a	2.2 a
WSB-Chunky	7.8 c	13.3 bc	19.2 bc	32.8 ab	46.3 **a**	42 **a**		-1.5 a	3.4 a	4.5 a	3.9 a	6.9 a	0.7 a

ANOVA	**F**	***p***	**SEM#**	**F**	***p***	**SEM#**
WSB-Fine						
Soil x Biochar rate	2.370	0.122	3.332	5.47	**0.014**	1.57
FSB-Fine						
Soil x Biochar rate	5.66	0.012	2.595	0.79	0.482	2.28
WB-Fine						
Soil x Biochar rate	5.01	0.018	2.998	0.78	0.473	1.39
WB-Chunky						
Soil x Biochar rate	8.90	**0.002**	3.232	0.10	0.903	1.99
WSB-Chunky						
Soil x Biochar rate	0.54	**0.005**	5.154	2.53	0.107	2.17

† WSB-Fine = Wheat straw fine fraction fast pyrolysis biochar; FSB-Fine = Flax straw fine fraction fast pyrolysis biochar; WB-Fine = Willow fine fraction slow pyrolysis biochar; WB-Chunky = Willow chunky fraction slow pyrolysis biochar; and FSB-Chunky = Wheat straw chunky fraction slow pyrolysis biochar

‡ All treatments received 50 kg N ha^{-1} as urea and 25 kg P_2O_5 ha^{-1} as monoammonium phosphate

§ For a crop, means (soil x biochar rate) with the same letter in the same row are not significantly different (p<0.05) (N = 24, n = 4). The multi-treatment comparisons were made using the Tukey's HSD method

Standard error of mean

Table A.5. Biochar amendment effects on recovery of applied phosphorus fertilizer by canola and wheat grown in rotation in CB-Brown and CLC-Black soil

Biochar type†	CANOLA							WHEAT					
	CB-Brown Soil‡			CLC-Black soil‡				CB-Brown Soil			CLC-Black soil		
	Biochar (t ha^{-1})			Biochar (t ha^{-1})				Biochar (t ha^{-1})			Biochar (t ha^{-1})		
	0	1	2	0	1	2		0	1	2	0	1	2
							%						
WSB-Fine	11.8 a§	8.5 a	10.5 a	8.0 a	11.8 a	9.6 a		0.0 a	1.3 a	0.6 a	2.5 a	-0.9 a	-0.8 a
FSB-Fine	4.7 a	5.9 a	4.5 a	4.5 a	4.8 a	4.7 a		0.5 a	1.0 a	0.7 a	1.6 a	0.0 a	1.2 a
WB-Fine	6.7 a	3.8 a	4.9 a	5.5 a	6.1 a	5.7 a		-0.2 a	0.9 a	0.6 a	0.7 a	0.6 a	0.0 a
WB-Chunky	2.2 bc	-0.7 c	2.3 bc	7.9 ab	10.9 a	11.6 a		1.9 a	2.2 a	2.8 a	2.1 a	1.0 a	1.5 a
WSB-Chunky	1.5 b	6.3 ab	5.0 ab	11.1 ab	12.0 a	9.3 ab		1.6 ab	3.1 a	1.0 ab	4.1 a	-2.6 b	-2.7 b
ANOVA		**F**	***p***		**SEM#**				**F**	***p***		**SEM#**	
WSB-Fine													
Soil x Biochar rate		3.17	0.066		1.437				2.95	0.078		1.027	
FSB-Fine													
Soil x Biochar rate		0.24	0.786		0.995				0.80	0.463		0.859	
WB-Fine													
Soil x Biochar rate		1.97	1.168		0.890				1.78	0.197		0.433	
WB-Chunky													
Soil x Biochar rate		2.25	0.134		1.373				0.85	0.443		0.612	
WSB-Chunky													
Soil x Biochar rate		0.79	0.467		2.238				6.65	0.007		1.167	

† WSB-Fine = Wheat straw fine fraction fast pyrolysis biochar; FSB-Fine = Flax straw fine fraction fast pyrolysis biochar; WB-Fine = Willow fine fraction slow pyrolysis biochar; WB-Chunky = Willow chunky fraction slow pyrolysis biochar; and FSB-Chunky = Wheat straw chunky fraction slow pyrolysis biochar

‡ All treatments received 50 kg N ha^{-1} as urea and 25 kg P_2O_5 ha^{-1} as monoammonium phosphate

§ For a crop, means (soil x biochar rate) with the same letter in the same row are not significantly different (p<0.05) (N = 24, n = 4). The multi-treatment comparisons were made using the Tukey's HSD method

Standard error of mean

Table A.6. Soil extractable nitrate concentration (mg NO_3^--N kg^{-1}) in biochar amended CB-Brown and CLC-Black soil

Biochar type‡	NO_3^--N (mg kg^{-1})†					
	CB-Brown Soil§			CLC-Black soil§		
	Biochar (t ha^{-1})			Biochar (t ha^{-1})		
	0	1	2	0	1	2
WSB-Fine	2.1 a¶	1.9 a	2.5 a	1.9 a	1.4 a	2.1 a
FSB-Fine	4.6 a	4.2 ab	1.8 ab	2.0 ab	2.5 ab	1.6 b
WB-Fine	0.8 a	0.7 a	2.3 a	2.1 a	2.1 a	1.7 a
WB-Chunky	1.0 a	0.0 b	0.3 b	1.2 a	1.5 a	1.3 a
WSB-Chunky	2.6 a	2.7 a	2.9 a	2.8 a	3.0 a	2.8 a
ANOVA		**F**	***p***		**SEM#**	
WSB-Fine						
Soil x Biochar rate		0.25	0.783		0.275	
FSB-Fine						
Soil x Biochar rate		1.88	0.182		0.622	
WB-Fine						
Soil x Biochar rate		2.24	0.135		0.514	
WB-Chunky						
Soil x Biochar rate		14.14	**0.002**		0.126	
WSB-Chunky						
Soil x Biochar rate		0.26	0.776		0.255	

† Extractable NO_3^--N

‡ WSB-Fine = Wheat straw fine fraction fast pyrolysis biochar; FSB-Fine = Flax straw fine fraction fast pyrolysis biochar; WB-Fine = Willow fine fraction slow pyrolysis biochar; WB-Chunky = Willow chunky fraction slow pyrolysis biochar; and FSB-Chunky = Wheat straw chunky fraction slow pyrolysis biochar

§ All All treatments received 50 kg N ha^{-1} as urea and 25 kg P_2O_5 ha^{-1} as monoammonium phosphate

¶ Means (soil x biochar rate) with the same letter in the same row are not significantly different (p<0.05) (N = 12, n = 4). The multi-treatment comparisons were made using the Tukey's HSD method

Standard error of mean

Table A.7. Soil extractable phosphate concentrations (mg PO_4^+-P kg^{-1}) in biochar amended CB-Brown and CLC-Black soil

Biochar type‡	PO_4^+-P (mg kg^{-1})†					
	CB-Brown soil§			CLC-Black soil§		
	Biochar (t ha^{-1})			Biochar (t ha^{-1})		
	0	1	2	0	1	2
WSB-Fine	15.0 a¶	15.3 a	13.1 b	9.8 c	10.0 c	8.3 c
FSB-Fine	18.6 a	15.6 b	16.0 b	11.8 c	10.3 c	11.9 c
WB-Fine	15.0 a	14.8 a	15.6 a	11.2 b	11.8 b	11.6 b
WB-Chunky	18.8 b	21.6 **a**	20.4 **a**	7.2 c	5.5 d	5.7 cd
WSB-Chunky	17.2 b	21.8 **a**	17.1 **a**	8.7 c	7.5 c	7.0 c
ANOVA		**F**	***p***		**SEM#**	
WSB-Fine						
Soil x Biochar rate		0.29	0.752		0.372	
FSB-Fine						
Soil x Biochar rate		7.10	**0.005**		0.356	
WB-Fine						
Soil x Biochar rate		0.62	0.551		0.504	
WB-Chunky						
Soil x Biochar rate		23.39	**<0.0001**		0.340	
WSB-Chunky						
Soil x Biochar rate		5.97	**0.010**		0.873	

† Extractable PO_4^+-P

‡ WSB-Fine = Wheat straw fine fraction fast pyrolysis biochar; FSB-Fine = Flax straw fine fraction fast pyrolysis biochar; WB-Fine = Willow fine fraction slow pyrolysis biochar; WB-Chunky = Willow chunky fraction slow pyrolysis biochar; and FSB-Chunky = Wheat straw chunky fraction slow pyrolysis biochar

§ All All treatments received 50 kg N ha^{-1} as urea and 25 kg P_2O_5 ha^{-1} as monoammonium phosphate

¶ Means (soil x biochar rate) with the same letter in the same row are not significantly different (p<0.05) (N = 12, n = 4). The multi-treatment comparisons were made using the Tukey's HSD method

Standard error of mean

Table A.8. Biochar amendment effects on soil pH in CB-Brown and CLC-Black soil

Biochar type‡	pH†					
	CB-Brown soil§			CLC-Black soil§		
	Biochar (t ha^{-1})			Biochar (t ha^{-1})		
	0	1	2	0	1	2
WSB-Fine	8.0 a¶	8.0 a	8.0 a	6.7 b	6.7 b	6.7 b
FSB-Fine	7.9 a	7.9 a	7.9 a	6.7 b	6.7 b	6.8 b
WB-Fine	7.9 a	7.9 a	7.9 a	6.8 b	6.6 c	6.7 bc
WB-Chunky	7.5 a	7.5 a	7.5 a	6.6 b	6.6 b	6.6 b
WSB-Chunky	7.4 a	7.5 a	7.5 a	6.4 b	6.5 b	6.4 b
ANOVA		**F**	***p***		**SEM#**	
WSB-Fine						
Soil x Biochar rate		0.02	0.977		0.030	
FSB-Fine						
Soil x Biochar rate		0.85	0.445		0.021	
WB-Fine						
Soil x Biochar rate		6.45	**0.008**		0.025	
WB-Chunky						
Soil x Biochar rate		1.86	0.184		0.025	
WSB-Chunky						
Soil x Biochar rate		2.14	0.146		0.027	

† pH of a 1:2 (soil:water) extract

‡ WSB-Fine = Wheat straw fine fraction fast pyrolysis biochar; FSB-Fine = Flax straw fine fraction fast pyrolysis biochar; WB-Fine = Willow fine fraction slow pyrolysis biochar; WB-Chunky = Willow chunky fraction slow pyrolysis biochar; and FSB-Chunky = Wheat straw chunky fraction slow pyrolysis biochar

§ All All treatments received 50 kg N ha^{-1} as urea and 25 kg P_2O_5 ha^{-1} as monoammonium phosphate

¶ Means (soil x biochar rate) with the same letter in the same row are not significantly different (p<0.05) (N = 12, n = 4). The multi-treatment comparisons were made using the Tukey's HSD method

Standard error of mean

Table A.9. Biochar amendment effects on soil organic carbon (OC) in a CB-Brown and CLC-Black soil

Biochar type†	OC (%) ‡					
	CB-Brown soil§			CLC-Black soil§		
	Biochar (t ha^{-1})			Biochar (t ha^{-1})		
	0	1	2	0	1	2
WSB-Fine	1.5 b¶	1.6 b	1.6 b	4.8 a	4.7 a	4.8 a
FSB-Fine	1.5 b	1.7 b	1.7 b	4.7 a	4.9 a	4.9 a
WB-Fine	1.5 b	1.6 b	1.7 b	4.4 a	4.4 a	4.6 a
WB-Chunky	2.0 b	2.2 b	2.2 b	4.5 a	4.7 a	4.6 a
WSB-Chunky	2.2 b	2.2 b	2.2 b	4.6 a	4.4 a	4.7 a
ANOVA		**F**	***p***		**SEM#**	
WSB-Fine						
Soil x Biochar rate		0.19	0.825		0.084	
FSB-Fine						
Soil x Biochar rate		0.07	0.936		0.078	
WB-Fine						
Soil x Biochar rate		0.23	0.793		0.080	
WB-Chunky						
Soil x Biochar rate		0.59	0.566		0.122	
WSB-Chunky						
Soil x Biochar rate		2.30	0.129		0.085	

† WSB-Fine = Wheat straw fine fraction fast pyrolysis biochar; FSB-Fine = Flax straw fine fraction fast pyrolysis biochar; WB-Fine = Willow fine fraction slow pyrolysis biochar; WB-Chunky = Willow chunky fraction slow pyrolysis biochar; and FSB-Chunky = Wheat straw chunky fraction slow pyrolysis biochar

‡ % soil organic carbon content

§ All treatments received 50 kg N ha^{-1} as urea and 25 kg P_2O_5 ha^{-1} as monoammonium phosphate

¶ Means (soil x biochar rate) with the same letter in the same row are not significantly different (p<0.05) (N = 12, n = 4). The multi-treatment comparisons were made using the Tukey's HSD method;

Standard error of mean

7.2 Appendix B: Biochar effects on crop above-ground biomass and soil moisture content in a Field experiment

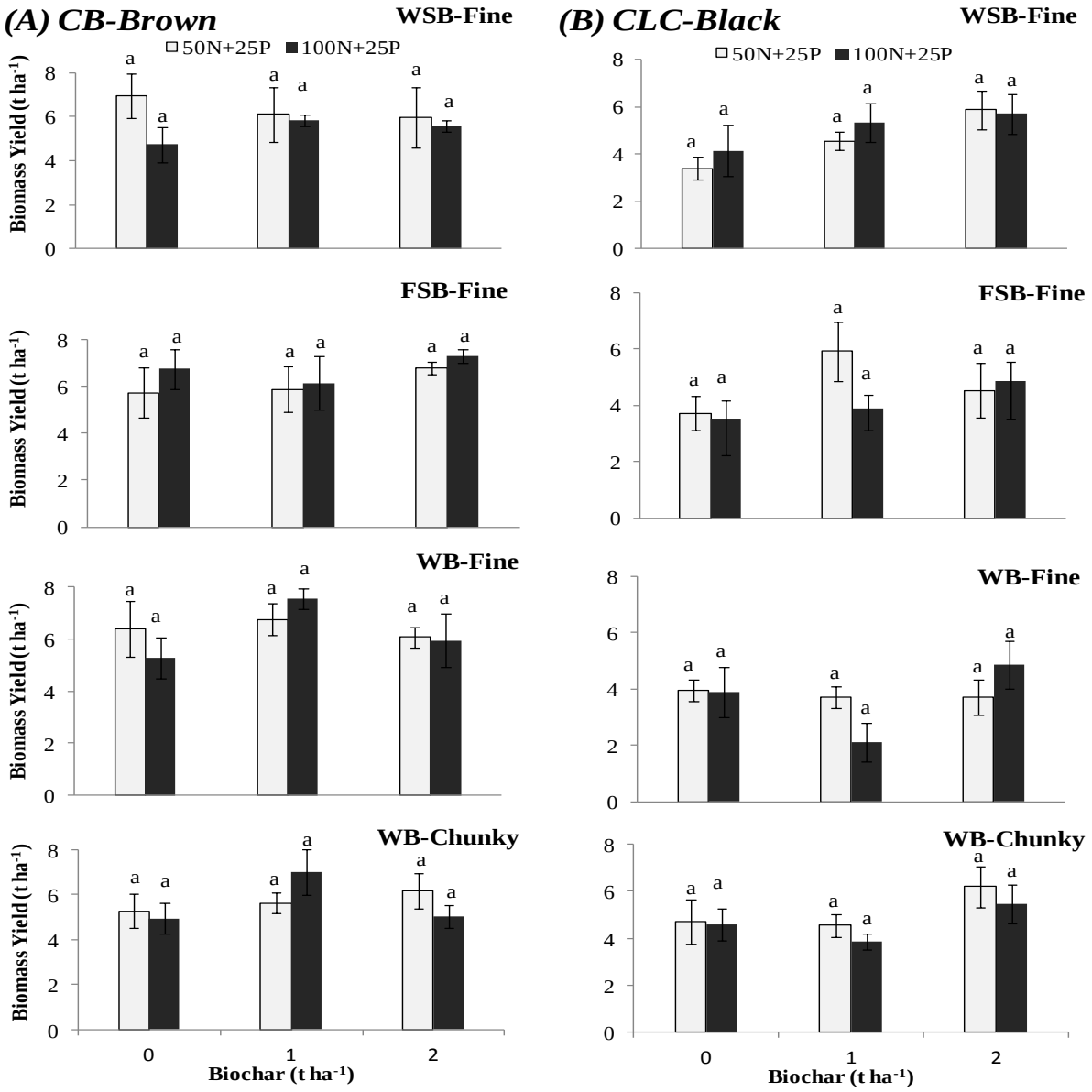

Fig. B.1. Mean total above-ground biomass yield (t ha^{-1}) of canola grown in the first year as a first crop in a rotation in biochar amended (A) CB-Brown and (B) CLC-Black soil in a field site experiment. Error bars are standard error of mean (biochar rate x fertilizer treatment) with N = 24 and n = 4. (WSB-Fine = Wheat straw fine fraction fast pyrolysis biochar; FSB-Fine = Flax straw fine fraction fast pyrolysis biochar; WB-Fine = Willow fine fraction slow pyrolysis biochar; WB-Chunky = Willow chunky fraction slow pyrolysis biochar). For a soil and biochar type, means with different letters are significantly different (Tukey's HSD, $p<0.05$)

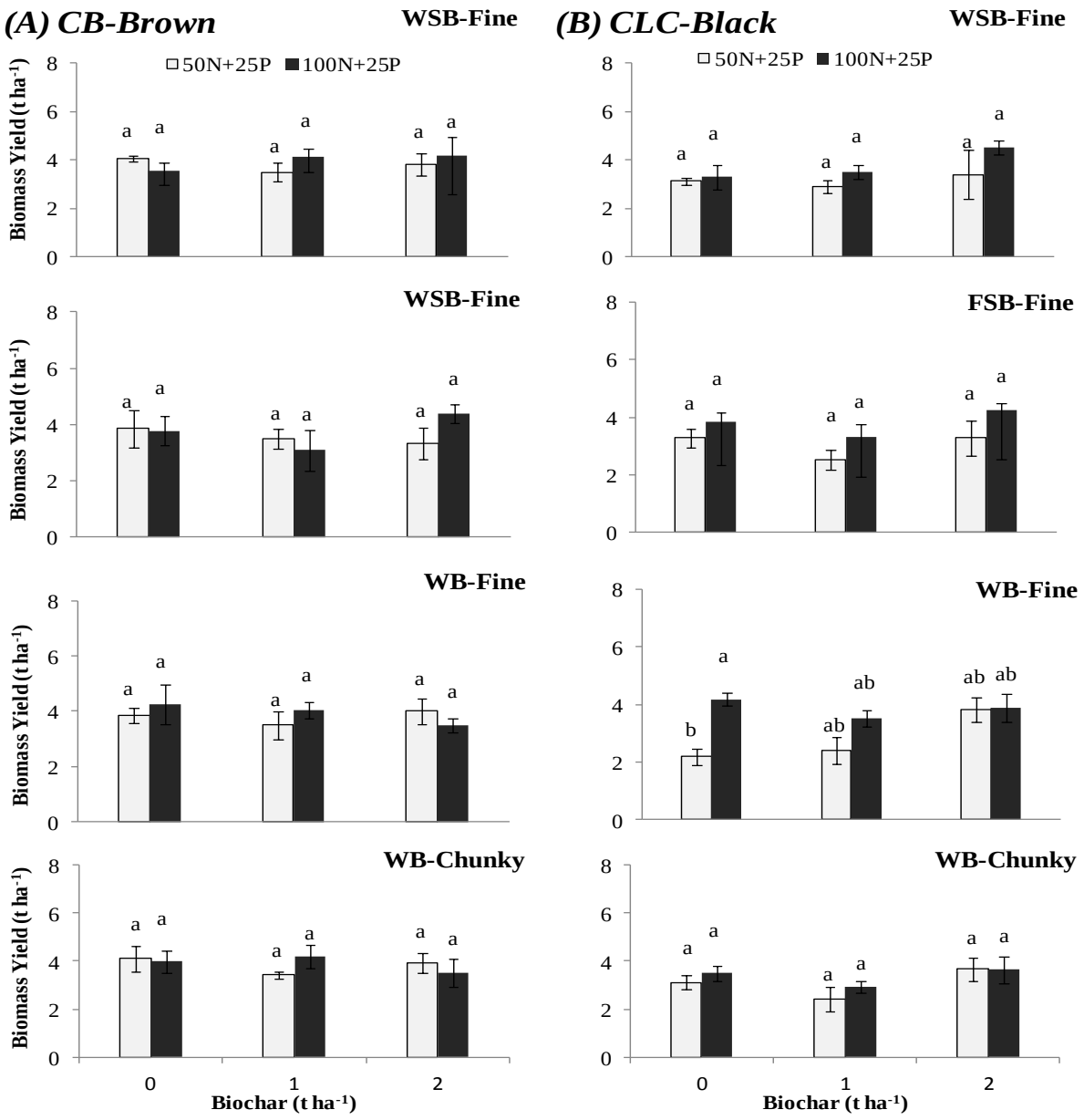

Fig. B.2. Mean total above-ground biomass yield (t ha^{-1}) of wheat grown in the second year as a second crop in a rotation in biochar amended (A) CB-Brown and (B) CLC-Black soil in a field site experiment. Error bars are standard error of mean (biochar rate x fertilizer treatment) with N = 24 and n = 4. (WSB-Fine = Wheat straw fine fraction fast pyrolysis biochar; FSB-Fine = Flax straw fine fraction fast pyrolysis biochar; WB-Fine = Willow fine fraction slow pyrolysis biochar; WB-Chunky = Willow chunky fraction slow pyrolysis biochar). For a soil and biochar type, means with different letters are significantly different (Tukey's HSD, $p<0.05$)

Table B.1. Soil moisture (%) by weight of different depths in biochar amended CB-Brown soil

Soil depth	Biochar type†	0N+0P‡			100N+25P§			BR x FT¶		
		Biochar rate (t ha^{-1})			Biochar rate (t ha^{-1})			F	*p*	SEM#
		0	1	2	0	1	2			
		%								
0-15 cm	WSB-Fine	8.9 A a††	7.9 A a	6.1 A a	6.8 A a	6.9 A a	6.1 A a	0.28	0.760	1.340
	FSB-Fine	8.8 A a	8.8 A a	8.9 A a	10.8 A a	7.1 A a	6.6 A a	0.76	0.482	1.848
	WB-Fine	11.1 A a	9.1 A a	6.2 A a	7.1 A a	6.6 A a	6.4 A a	0.51	0.609	2.122
	WB-Chunky	11.3 A a	9.9 A a	7.8 A a	6.3 A a	6.8 A a	6.5 A a	0.35	0.709	2.298
15-30 cm	WSB-Fine	13.7 A a	13.8 A a	14.5 A a	11.0 A a	10.5 AB a	10.1 A a	0.04	0.964	2.719
	FSB-Fine	13.6 A a	14.2 A a	14.8 A a	9.8 A a	9.0 AB a	9.4 A a	0.16	0.852	1.829
	WB-Fine	12.0 A a	13.4 A a	10.3 A a	10.4 A a	**6.9 B a**	9.3 A a	1.5	0.256	1.777
	WB-Chunky	11.5 A a	13.6 A a	12.6 A a	9.8 A a	**13.8 A a**	8.1 A a	0.89	0.428	1.777
30-60 cm	WSB-Fine	15.9 A a	16.4 a	16.6 A a	11.3 A a	12.4 A a	13.5 A a	0.08	0.923	1.781
	FSB-Fine	**14.3 A a**	12.6 A ab	**13.7 A a**	10.3 A ab	**8.2 A b**	11.0 A ab	0.29	0.753	1.196
	WB-Fine	15.6 A a	16.9 A a	12.3 A a	11.3 A a	10.4 A a	10.4 A a	0.65	0.536	1.981
	WB-Chunky	14.5 A a	14.2 A a	14.9 A a	15.3 A a	8.8 A a	12.9 A a	1.35	0.288	1.970

† WSB-Fine = Wheat straw fine fraction fast pyrolysis biochar; FSB-Fine = Flax straw fine fraction fast pyrolysis biochar; WB-Fine = Willow fine fraction slow pyrolysis biochar; and WB-Chunky = Willow chunky fraction slow pyrolysis biochar

‡ No N and P fertilizer added

§ 100 kg N ha^{-1} as urea and 25 kg P_2O_5 ha^{-1} as monoammonium phosphate

¶ Biochar rate (BR) and Fertilizer treatment (FT) interaction

Standard error of mean

†† For a depth, means (biochar type, N = 16, n = 4)) with the same upper case letter in the same column and means (biochar rate x fertilizer treatment, N=24, n=4) with the same lower case letter in the same row are not significantly different (p<0.05) . The multi-treatment comparisons were made using the Tukey's HSD method

Table B.2. Soil moisture (%) by weight of different depths in biochar amended CLC-Black soil

Soil depth	Biochar type†	0N+25P‡ Biochar rate (t ha^{-1}) 0	1	2	100N+25P§ Biochar rate (t ha^{-1}) 0	1	2	BR x FT¶ F	*p*	SEM#
		%								
0-15 cm	WSB-Fine	24.6 A a††	21.7 A a	26.7 A a	23.9 A a	20.1 B a	24.1 A a	0.08	0.923	2.343
	FSB-Fine	23.2 A a	24.4 A a	22.5 A a	22.9 AB a	21.2 B a	24.1 A a	3.43	0.055	0.903
	WB-Fine	22.7 AB a	23.1 A a	23.4 A a	22.6 AB a	25.2 A a	22.7 A a	1.66	0.223	0.840
	WB-Chunky	19.3 A a	24.5 A a	26.9 A a	19.8 B a	23.2 AB a	21.6 A a	0.92	0.419	2.223
15-30 cm	WSB-Fine	26.6 AB a	27.4 AB a	25.3 A a	30.6 **A** a	25.1 A a	29.2 A a	1.49	0.257	2.208
	FSB-Fine	28.7 A a	27.7 A ab	23.9 A ab	20.8 B **b**	**25.8 A ab**	**27.1 A ab**	6.63	0.007	1.542
	WB-Fine	25.2 AB a	25.7 B a	25.5 A a	24.8 AB a	24.4 A a	26.5 A a	0.83	0.454	0.863
	WB-Chunky	22.5 B a	26.3 AB a	25.6 A a	22.5 B a	28.5 A a	23.0 A a	0.52	0.603	2.379
30-60 cm	WSB-Fine	29.8 A a	29.3 A a	28.8 A a	26.5 A a	29.7 A a	26.2 A a	0.68	0.519	1.678
	FSB-Fine	28.6 A a	27.6 A ab	27.5 A a	26.1 A ab	27.0 A b	27.0 A ab	1.19	0.328	0.730
	WB-Fine	26.7 A a	29.4 A a	26.8 A a	28.1 A a	26.9 A a	26.6 A a	1.87	0.1889	1.009
	WB-Chunky	27.2 A a	26.4 A a	24.2 A a	25.9 A a	24.4 A a	25.8 A a	0.81	0.4626	1.560

† WSB-Fine = Wheat straw fine fraction fast pyrolysis biochar; FSB-Fine = Flax straw fine fraction fast pyrolysis biochar; WB-Fine = Willow fine fraction slow pyrolysis biochar; and WB-Chunky = Willow chunky fraction slow pyrolysis biochar

‡ 50 kg N ha-1 as urea and 25 kg P_2O_5 ha^{-1} as monoammonium phosphate

§ 100 kg N ha^{-1} as urea and 25 kg P_2O_5 ha^{-1} as monoammonium phosphate

¶ Biochar rate (BR) and Fertilizer treatment (FT) interaction

Standard error of mean

†† For a depth, means (biochar type, N = 16, n = 4)) with the same upper case letter in the same column and means (biochar rate x fertilizer treatment, N=24, n=4) with the same lower case letter in the same row are not significantly different (p<0.05) . The multi-treatment comparisons were made using the Tukey's HSD method